

Identification of High Confidence Nuclear Forensics Signatures

*Results of a Coordinated Research Project
and Related Research*



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IDENTIFICATION OF HIGH CONFIDENCE NUCLEAR FORENSICS SIGNATURES

RESULTS OF A COORDINATED RESEARCH PROJECT
AND RELATED RESEARCH

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2017

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FOREWORD

As a means to prevent and respond to a nuclear security event, nuclear forensics provides information on the origin and history of nuclear and other radioactive materials out of regulatory control in the context of legal proceedings under international or national law relating to nuclear security. By bridging nuclear science, law enforcement and nuclear security, nuclear forensics depends on diverse disciplines and technical capabilities. The strength of a nuclear forensic examination is not contingent upon a single technology but is instead derived from demonstrated confidence in conclusions following laboratory analysis and data interpretation. Innovation in nuclear forensic methodologies is driven by science and research. For this reason, the IAEA has prioritized coordinated research projects (CRPs) in nuclear forensics as a means to provide scientifically validated and objective solutions to promote confidence in the conclusions following a nuclear forensic examination. In addition, CRPs provide a mechanism to build confidence in nuclear forensics by sharing the experience of researchers and examiners from around the world.

As States utilize nuclear forensics as a preventive and response to a nuclear security event, confidence in the findings from a nuclear forensic examination is essential. Because nuclear forensics supports law enforcement investigations and nuclear security vulnerability assessments, the scientific methods supporting the examination need to be fully validated and defensible.

Recent research focuses on the identification of nuclear forensics data characteristics (or signatures), their accurate measurement and prediction, the controls over their incorporation and persistence across the nuclear fuel cycle, and how signatures can be exploited as part of a nuclear forensic examination.

The outcomes of this CRP highlight the development of new nuclear forensic analytical techniques to include nuclear and radioactive material age dating (i.e. time of production), morphology studies of nuclear materials to trace origin and history, investigation of nuclear microparticles, the role of modelling to identify the origin of spent nuclear fuels, as well as the application of rare earth elements to differentiate uranium ores and concentrates. Researchers note that multiple signatures are necessary for building confidence in the conclusions reached by nuclear forensic examiners.

The present CRP, Identification of High Confidence Nuclear Forensics Signatures for the Development of National Nuclear Forensics Libraries, was conceived in 2011, commenced in 2013 and ended in 2016. Two research coordination meetings (RCMs) were convened. K. Smith (Australian Nuclear Science and Technology Organisation, ANSTO) chaired the first RCM, held at the IAEA in December 2014. E. Keegan (ANSTO) chaired the second RCM, held in July 2016 at the Centre for Energy Research, Budapest, and was instrumental in the technical review of this publication. Their leadership fostered a crucial scientific exchange, which has contributed to advancing the state of practice in the field of nuclear forensics.

The IAEA acknowledges the Member States' chief scientific investigators, their collaborators and the many contributors to the CRP and the related research for their assistance in the preparation of this publication. The IAEA officer responsible for this publication was D.K. Smith of the Division of Nuclear Security.

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SUMMARY

1. INTRODUCTION

This technical publication provides scientific results of an IAEA Coordinated Research Project “Identification of High Confidence Nuclear Forensics Signatures for the Development of National Nuclear Forensics Libraries” conducted between 2013 and 2016 to study the scientific basis for the identification, measurement and interpretation of nuclear forensic data characteristics, or signatures, helpful to the interpretation of the results of a nuclear forensics examination. Additionally the publication also includes three related nuclear forensic reports not included in the CRP but undertaken in parallel by researchers of the Russian Federation.

Innovative nuclear forensics research is important to optimize determinations of the origin and history of nuclear and other radioactive materials encountered out of regulatory control, to link nuclear security events through nuclear forensic findings and to provide confidence in the results of a nuclear forensics examination. By providing the recent results of coordinated research involving leading international laboratories, this publication seeks to bridge different expertise in analytical and interpretative tools as well as the varied experience of investigators with nuclear forensics applied to the use, production and storage of nuclear and radioactive materials. A range of nuclear and radioactive materials were investigated in this research including environmental samples, material from the front end of the fuel cycle (uranium ores and ore concentrates), spent nuclear fuel as well as radioactive sources.

The publication provides information on nuclear forensics signatures useful to identify and source materials, analytical methods for their measurement in bulk or particulate samples, predictive approaches to identify signatures not easily measured in the laboratory (i.e spent nuclear fuels) and use of signatures in a system of national identification of nuclear and radioactive materials to include a national nuclear forensic library. In addition the publication emphasizes that an examination benefits from the application of multiple measurements to mutually reinforce laboratory analysis. The publication may assist those involved in the design and conduct of a nuclear forensics examination, experts responsible for the findings derived from these analyses as well as for specialists contemplating a national system for the nuclear forensics identification of nuclear and other radioactive materials to include the development of a national nuclear forensic library. The publication further aims to raise technical developments in the field to develop, sustain and utilize nuclear forensics as part of a nuclear security infrastructure.

2. BACKGROUND

Nuclear forensics assists States in meeting their nuclear security responsibilities by providing information on the origin and history of nuclear and other radioactive material out of regulatory control consistent with national laws and international legal instruments. Nuclear forensics has been applied to investigations of nuclear security events involving the unauthorized possession or use of nuclear and other radioactive materials involving law enforcement investigations and nuclear security assessments.

Reports of nuclear and other radioactive materials out of regulatory control continue to occur with regularity. From 1993 to the end of 2016, the IAEA’s Incident and Trafficking Database (ITDB) compiled 3068 confirmed incidents of nuclear and other radioactive material out of regulatory control. Of heightened concern, recent incidents point to organized networks of sellers and buyers for this material. In this context nuclear forensics is essential for preventing, detecting and responding to criminal and unauthorized acts involving nuclear and other radioactive materials.

In order to keep abreast of the evolving and continual threat, innovation and a commitment to scientific solutions is necessary to maintain the viability of nuclear forensics as an effective component of a State’s nuclear security infrastructure. As more States develop nuclear forensics capabilities, the need for validated scientific techniques and reliable measurements and interpretation grows proportionally. Law enforcement and other responsible authorities must have full confidence in the science supporting

results returned from a nuclear forensics examination. The challenge is considerable; nuclear forensic laboratories need to be capable of analysing small quantities of uranium, plutonium, transuranic elements, as well as sealed and unsealed radioactive materials. Both un-irradiated and irradiated materials may be encountered. The present research further offers specialized techniques to allow measurements of bulk and particulate samples of uranium as well as plutonium and other radionuclides. Outcomes demonstrate that case studies benefit from the application of multiple measurements to build confidence in the conclusions from a nuclear forensic examination.

Interpretation of nuclear forensic signatures is a comparative discipline where results from the analysis of unknown samples are compared against populations of known materials. The ability to reliably determine the origin and history of nuclear and other radioactive materials depends upon access to relevant sample materials, the identification of priority signatures, high confidence measurements or predictions, and the ability to perform intercomparisons between data collected on an unknown sample and a knowledge or data-base of known material to potentially include a national nuclear forensics library.

3. OBJECTIVE

This publication reflects recent research activities undertaken to identify of important nuclear forensics signatures, facilitate their accurate measurement and prediction, elucidate the controls over the incorporation and persistence of nuclear forensic signatures across the nuclear fuel cycle, and advance how signatures can be used as part of a nuclear forensic examination to support law enforcement investigations or nuclear security vulnerability assessments. A priority was resolving geologic signatures of uranium ores and ore concentrates from nuclear fuel cycle processing signatures in nuclear fuels and irradiated materials. The results published here may assist in the development of an identification scheme for nuclear and other radioactive materials incorporating knowledge bases utilized by subject matter experts (SMEs). The findings from the CRP complement additional results included here derivative from individual nuclear forensic research contracts with investigators from the Russian Federation. This publication hopes to inform awareness and understanding of nuclear forensics as well as the importance of the science of signatures as they contribute to robust nuclear forensic findings.

4. SCOPE

This TECDOC presents research papers that address the identification, measurements and interpretation of isotopic, chemical and physical signatures important to a nuclear forensics examination supporting the investigation of a nuclear security event. The document reflects the outcomes of research requirements and institutional capabilities of thirteen leading laboratories involved in the conduct of a nuclear forensics examination. The publication presents results from chief scientific investigators on the incorporation of nuclear forensics signatures in the nuclear fuel cycle and their persistence as well as their ensuing methods for their measurement and interpretation. This publication disseminates studies involving arrays of materials to include uranium ores, uranium ore concentrates, nuclear fuels, spent nuclear fuels and radioactive sources.

The impact of the CRP highlights the importance of material characteristics and access to relevant and representative sample materials and/or reliable nuclear data for predictive modelling. A key challenge in nuclear forensic signature investigation is the alteration or removal of signatures diagnostic of unique stages of the nuclear fuel cycle as a result of the blending of materials from different origins. Intercomparisons between data collected on nuclear and radioactive material of interest and a knowledge or data-base of known material is required for nuclear forensic identifications and interpretation. The role of subject matter experts is important to understanding signatures and the scientific models on which these are based. Involvement of SMEs is essential for the use of a national system for the identification of nuclear and other radioactive materials to include the development of a national nuclear forensic library.

5. BRIEF REVIEW OF RESEARCH PAPERS

This section summarizes the research papers provided by chief scientific investigators of the CRP and the research activities undertaken by the Russian Federation.

Paper 1: High confidence nuclear forensics signatures with a focus on uranium ores and ore concentrates are important for the development of a national nuclear forensics library. Analytical techniques to include electron imaging, molecular spectroscopy, inductively coupled plasma mass spectroscopy, thermogravimetric analysis and neutron activation analysis were applied to differentiate uranium obtained from different sources. This work “Investigation of Various Signatures and Their Application to the Provenancing of Materials at the Front End of the Nuclear Fuel Cycle” was completed by the Australian Nuclear Science and Technology Organisation and Flinders University, Australia.

Paper 2: Environmental sampling, with established application to nuclear nonproliferation, was further applied to support nuclear forensic examinations. New techniques and protocols for extraction and measurements of nuclear materials show promise. Remote sensing research guides optimization of a nuclear forensic analytical plan. “Identification of Nuclear Forensics Signatures in Environmental Samples” was reported by the Comissão Nacional de Energia Nuclear, Brazil.

Paper 3: In support of efforts to develop a national nuclear forensics library, Canadian researchers are identifying signatures on irradiated nuclear fuels to incorporate post-irradiation examination. The Canadian Nuclear Forensics Laboratories describe fuel data using isotopic ratio and fission product analyses in a paper entitled “Nuclear Forensics of Irradiated CANDU Fuel”.

Paper 4: Studies of rare earth elements, lead, strontium, neodymium, and sulfur isotopes, as well as the morphology of processed uranium-compounds, including UO_3 , UO_2 and UF_4 , provide insight into the persistence of nuclear forensics signatures in the processing of uranium ores to uranium ore concentrates as well as related refined materials. The European Commission’s Joint Research Centre, Karlsruhe, Germany reports progress in the paper “Propagation of Nuclear Forensics Signatures at the Front-End of the Fuel Cycle”.

Paper 5: The use of computer codes to discriminate simulated relative to actual commercial spent nuclear fuels of different provenance is effective in resolving enrichments in fuels from different reactor types. A companion study to model radiography applications used neutron and gamma beams to discriminate combinations of ^{235}U and ^{239}Pu within a cuboidal object. Research findings are reported as “Parameterization of Unknown Spent Nuclear Fuel from Nuclear Reactors in View of Identifying Origins” by the Democritus University of Thrace, Greece.

Paper 6: The analysis of nuclear and radioactive material samples seized out of regulatory control in Hungary contributes to national efforts to develop a national nuclear forensics library. The data characteristics from a nuclear forensics examination are organized in prototype relational database that allows direct access from laboratories and field radiological crime scenes. The subject work is contained in the paper “Establishment of a National Library for Nuclear Forensics Purposes in Hungary” by the Centre for Energy Research in Hungary.

Paper 7: Access to samples from successive closed stages of the nuclear fuel cycle as well as utilization of analytical instrumentation coupled with subject matter expertise contributes to India’s national efforts to develop a national nuclear forensics library. “Mass Spectrometry, Radiometry and Other Analytical Techniques for Nuclear Forensics” is summary report contributed by the Bhabha Atomic Research Centre, India.

Paper 8: To better prepare Indonesia to establish a national nuclear forensics library, Indonesia is undertaking national efforts to study a range of nuclear materials to include those obtained from uranium mining, milling, refining processes, conversion, fuel fabrication, research reactors, spent fuel storage and handling of radioactive waste. Indonesia’s National Nuclear Energy Agency - BATAN characterization

efforts are reported in a paper entitled “Identification of High Confidence Nuclear Forensics Signatures, for Mining, Milling and Conversion Processes”.

Paper 9: Research into the signatures associated with strong activity ^{241}Am sources using gamma spectroscopy as well minimizing interferences associated with mass spectrometry measurements of the lanthanides supports nuclear forensic signature science. The Swedish Defense Research Agency completed this work with the title “Signatures for Nuclear Forensic Investigations”.

Paper 10: Using inductively coupled plasma mass spectrometry to measure isotope ratios and chemical concentrations from uranium mine and tailing effluents returns signatures important for the development of a national nuclear forensics library for South Africa. The North West University of South Africa reports initial research results on these analyses in “Resolving Nuclear Forensics Signatures from a Uranium and Thorium Mine in South Africa Using the ICP-MS Isotopic Ratio Technique”.

Paper 11: Studies to detect, localize and analyze uranium and plutonium microparticles in textiles and identify particle composition by autoradiography using the shape of tracks in polycarbonate detectors may be applied to studies involving nuclear materials encountered out of regulatory control. The report “Development of Techniques for Detection and Subsequent Analysis of Alpha-Emitting Microparticles on Fabrics” was contributed by the Laboratory for Microparticle Analysis of the Russian Federation.

Paper 12: The use of non destructive gamma spectrometry to rapidly identify uranium and plutonium in spent nuclear fuel utilizes the identification of long-lived fission products of ^{137}Cs , ^{134}Cs , ^{106}Ru , ^{144}Ce , ^{125}Sb , ^{154}Eu and ^{155}Eu to identify possible fuel origins. A research progress report submitted by the V.G. Khlopin Radium Institute of the Russian Federation is entitled “Development of a Gamma-Spectrometric Procedure for the Identification of Uranium and Plutonium in the Presence of Gamma Emitting Radionuclide Markers Indicative of Spent Nuclear Fuel (SNF) Out of Regulatory Control”.

Paper 13: Inductively coupled plasma mass spectrometry analysis of trace elements in uranium ore concentrates seized from incidents of illicit trafficking of nuclear materials is traditionally hampered by strong matrix effects. Dilution of the sample, the use of internal and external standards, and a chromatography method compensate for this effect. The paper “Development of the Trace Element Technique for the Measurement of the Characteristic Impurities of U_3O_8 for Identification Purposes in the Illicit Trafficking of Nuclear Materials” was authored by the A.A. Bochvar High Technology Research Institute of Inorganic Materials of the Russian Federation.

PAPERS PRESENTED

INVESTIGATION OF VARIOUS SIGNATURES AND THEIR APPLICATION TO THE PROVENANCING OF MATERIALS AT THE FRONT END OF THE NUCLEAR FUEL CYCLE

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1. INTRODUCTION

For this IAEA Coordinated Research Project (CRP), Australia (ANSTO and Flinders University) investigated various nuclear forensic signatures in material from the front end of the nuclear fuel cycle. Australia has a particular interest in uranium ores and uranium ore concentrates (UOCs); it possesses the world's largest easily minable resources of uranium bearing ore and is the world's third-ranking producer of UOC, behind Kazakhstan and Canada. As a radioactive powder and the starting material for production of nuclear fuel, UOC is of high interest for nuclear forensics.

2. WORK CONDUCTED

2.1 APPLICATION OF ANALYTICAL TECHNIQUES

A number of instrumental techniques were applied to UOC samples of known ore, mining or processing age to explore the value of the measurements to determine nuclear forensic signatures of either the origin of the material or its processing history. Scanning electron microscopy (SEM), visible/near infrared (Vis/NIR) diffuse reflectance spectroscopy (DRS) and transmission far-infrared (Far-IR) spectroscopy were applied at ANSTO. ANSTO also sought to develop the capability to measure the age of uranium bearing materials using the $^{231}\text{Pa}/^{235}\text{U}$ chronometer and quadrupole inductively coupled plasma mass spectrometry (qICP-MS). The thermal decomposition of UOCs was analysed via thermogravimetric analysis (TGA) at Flinders University using micro-Raman spectroscopy, X ray diffraction (XRD) and SEM to identify the different phases present within the original UOC, their respective thermal decomposition products and changes to the morphology as a function of increased temperature. Flinders University also analysed the rare earth elemental (REE) composition of uranium ore samples from Australian mines using neutron activation analysis (NAA). A summary of the techniques applied to UOCs is summarised in Table 1.

TABLE 1. A SUMMARY OF TECHNIQUES APPLIED TO UOCS AND/OR URANIUM ORES

Techniques	Information Obtained
SEM (and TEM)	Microstructural morphology and imaging
Vis/NIR (DRS) and Transmission Far-IR spectroscopy	Chemical compound
ICP-qMS of $^{233}\text{Pa}/^{231}\text{Pa}$	Age determination of uranium materials
Thermogravimetric analysis (TGA) and Micro-Raman spectroscopy & XRD	Phase composition and thermal decomposition products
Neutron activation analysis (NAA)	Elemental composition of U ore

Eight UOC samples and seven uranium ore samples from Australian mines were used in the course of this study. The UOC samples comprised of 3 samples each from Beverley and Ranger uranium mine (all sampled in/around 2004, each about 6 months apart), and 2 from Olympic Dam (sampled in 2005-2006, sampled 8 months apart). The colour of the UOC samples ranged from dark yellow in the case of Beverley, ($\text{UO}_4 \cdot n\text{H}_2\text{O}$) to dark green/black (U_3O_8 , Ranger and Olympic Dam). Of the Australian uranium ore samples, two samples were obtained from both Ranger and Olympic Dam, while a single sample was obtained from Beverley, Four Mile and Mary Kathleen, respectively.

2.2 SCANNING ELECTRON MICROSCOPY (SEM) and TRANSMISSION ELECTRON MICROSCOPY (TEM)

The eight UOC samples were examined by SEM in two ways; internal microstructure of the UOC grains was examined by mounting the samples in epoxy and polishing (and carbon coating to prevent accumulation of charge), and the external structural features of UOC grains were examined by adhering samples 'as received' to double-sided carbon tape (and coating with platinum).

As published earlier, internal structure and external morphology of UOC samples from each mine under study are shown in Fig. 1 and Fig. 2, respectively (microstructure was similar for all samples from the same mine) [1]. Different surficial and internal morphological features were present for each of the three mines which could be used to differentiate between different sources; in particular, the Ranger UOC exhibited an abundance of rod-like structures.

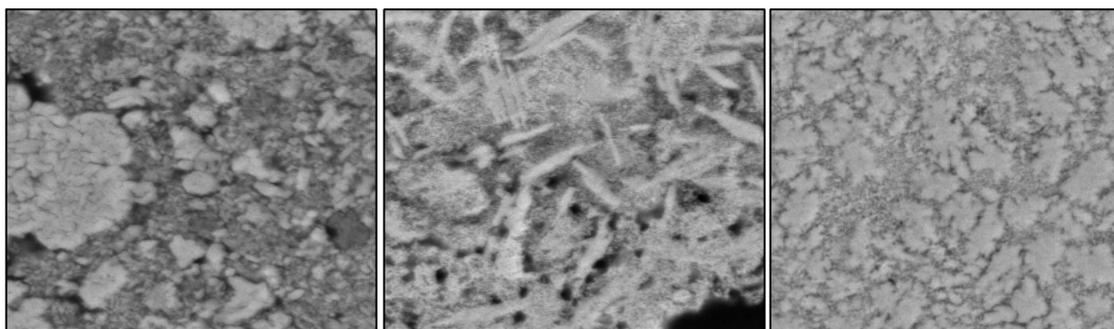


FIG 1. SEM images of epoxy mounted, polished and carbon coated UOC samples from Beverley (left), Ranger (centre) and Olympic Dam (right) at $\times 1500$ magnification ($15 \mu\text{m}$ image width).

The morphologies of the UOCs were also examined throughout the TGA analysis (see below) to investigate the effect temperature had on their distinct morphologies. The UOCs from each mine were found to behave quite similarly, irrespective of the atmosphere the samples were heated in (air or nitrogen), where they appeared unchanged in the 200/280 °C and 500 °C intermediate samples collected. In the samples heated to 1000 °C, all three UOCs appeared to have undergone a mild sintering, where the

particles had begun to fuse together, but not to the extent that their distinctive morphologies could not still be identified within the samples [2].

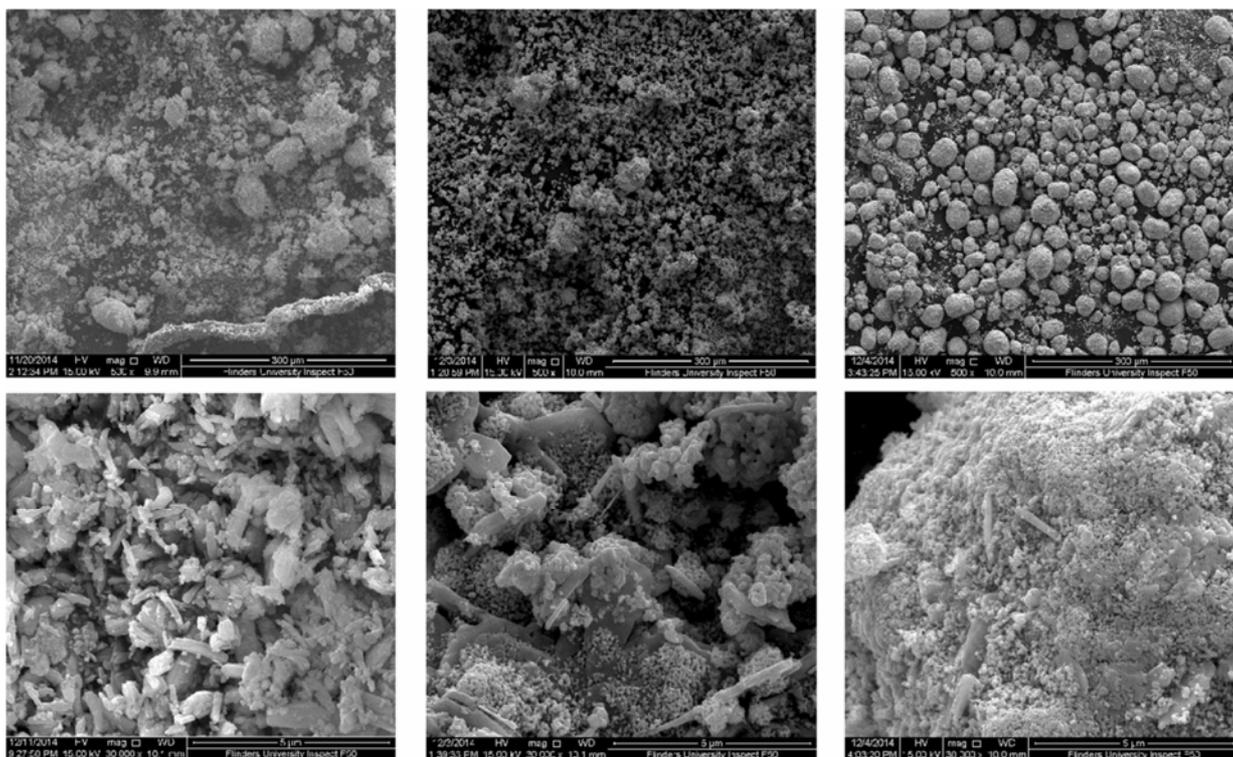


FIG 2. SEM images of UOC samples from Beverley (left), Ranger (centre) and Olympic Dam (right) at $\times 500$ (top row, scale bar is $300\ \mu\text{m}$) and $\times 30,000$ (bottom row, scale bar is $5\ \mu\text{m}$) magnification.

Transmission electron microscopy (TEM) was carried out upon the Olympic Dam sample only. The resulting TEM-EDS image provided elemental analysis of morphological microstructures and was of interest to further understand sample substructure. As a provenance technique for UOCs, it must be applied carefully since the small amount of sample analysed may not be representative of the bulk material.

2.3 VIS/NIR SPECTROSCOPY – DIFFUSE REFLECTANCE SPECTROSCOPY

Klunder et al. studied the DRS spectrum of a range of UOCs and found it to be a viable method to distinguish between different chemical compounds of uranium [3]. Diffuse reflectance has the advantage of being non-destructive with very minimal sample preparation. For the work presented here, each sample was simply ground and pressed into a sample cup and the reflectance of scattered VIS/IR light was measured. As published previously, the diffuse reflectance spectra were measured in the visible (400-700 nm) and near-IR (800-2500 nm) spectral regions (Fig. 3) and demonstrated that there were no major differences between Olympic Dam and Ranger, as expected, while Beverley was very different [1].

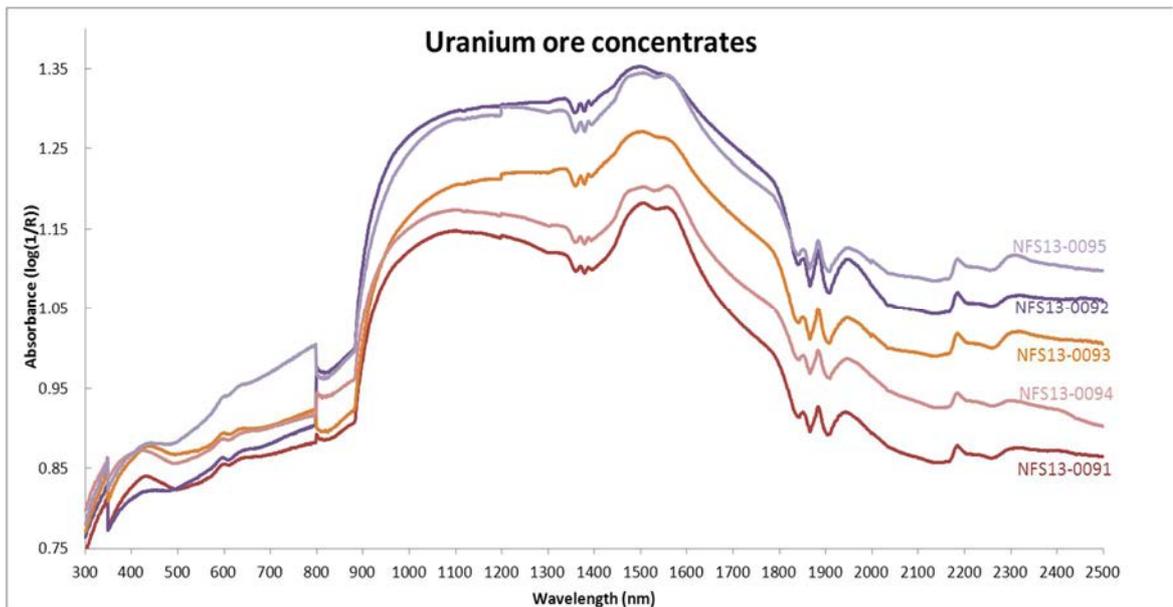
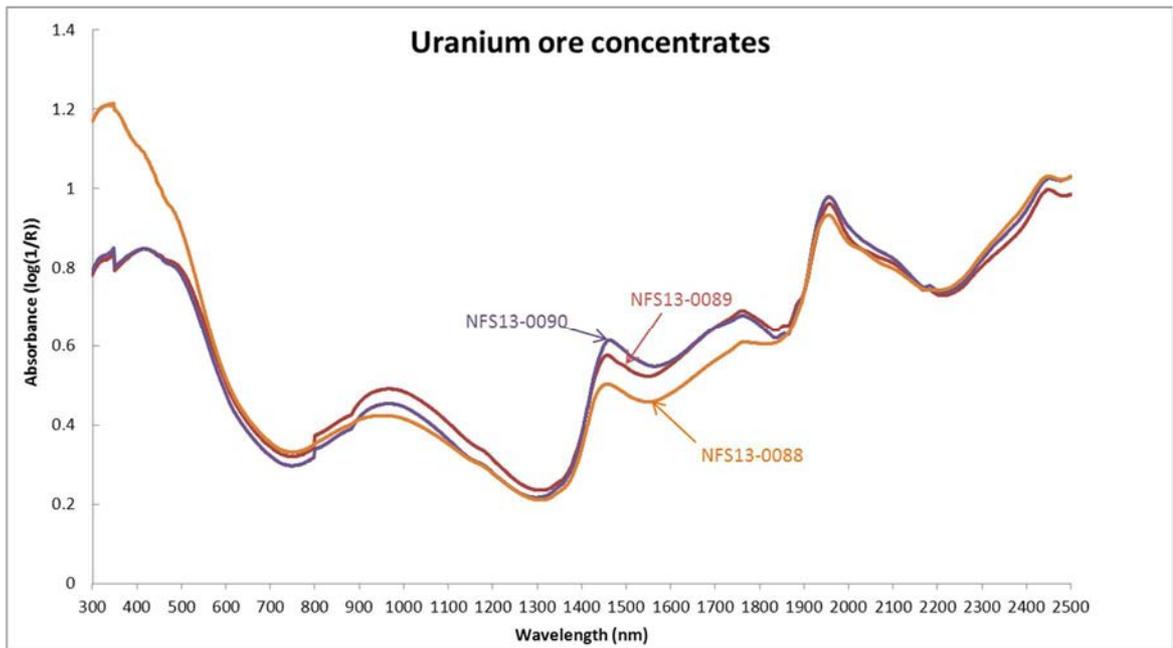


FIG 3. Full scan Vis/NIR spectra of Beverly UOCs ($UO_4 \cdot nH_2O$) (top) and Olympic Dam and Ranger UOCs (U_3O_8) (bottom, Olympic Dam (NFS13-0094 and 0095) and Ranger (NFS13-0091 to 0093)). Note grating changes at ~ 350 and 780 nm.

2.4 FAR-INFRARED (IR) SPECTROSCOPY

Far-IR spectra of the UOC samples were also obtained. Spectra were collected in transmission mode from 150 to 700 cm^{-1} (Fig. 4). As for DRS, the spectra for $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ were significantly different to U_3O_8 .

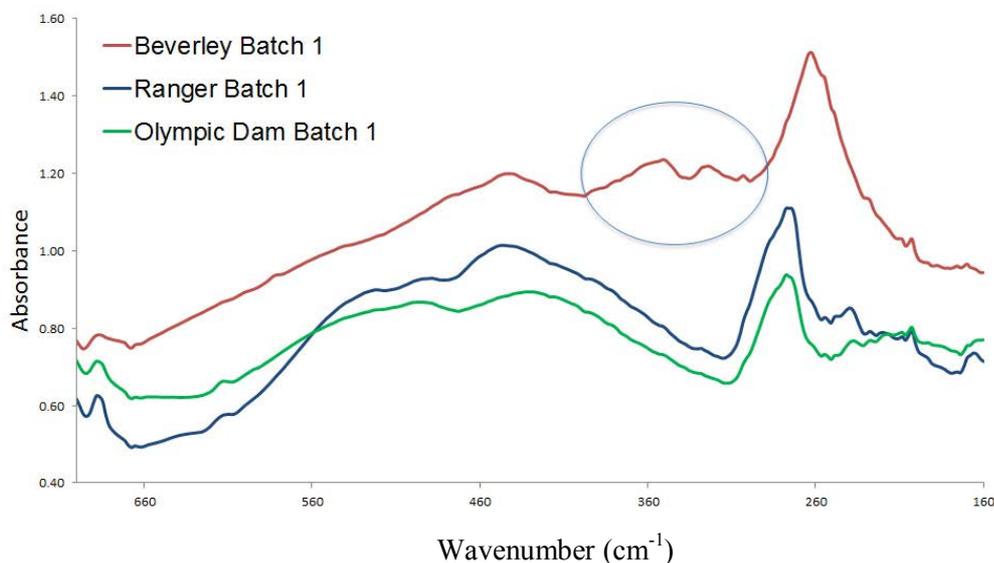


FIG 4. Transmission mode Far-IR spectra of Beverley, Olympic Dam and Ranger UOC (CsI disks). A region of particular difference between Beverley and the other two mines has been circled.

2.5 DEVELOPMENT OF THE CAPABILITY TO MEASURE $^{231}\text{Pa}/^{235}\text{U}$ FOR AGE DATING

Age determination is undoubtedly one of the most powerful nuclear forensic signatures and measurement of the age using two chronometers provides increased confidence in the analytical age measured. The Pa/U system is not commonly applied in nuclear forensic analyses due to complex Pa chemistry, the need for the non-natural ^{233}Pa spike for isotope dilution measurements and the need to analyse the radiochemically separated fractions quickly due to the short half-life of the ^{233}Pa (^{233}Pa half-life is 26.9 days, it decays via beta decay to ^{233}U). In this study, a procedure was developed to enable measurement of two chronometric systems ($^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$) using a single separation scheme.

Measurements of the Th and Pa fractions were made using quadrupole ICP-qMS. Investigations into the behaviour of ^{233}Pa versus ^{233}U found that they were similarly ionised, transported and detected during ICP-qMS measurement. This means that $^{231}\text{Pa}/^{233}\text{Pa}$ isotopic measurements do not need to be made soon after the column separation of Pa from U. This significantly simplifies the ICP-qMS spectrometric measurement for the $^{231}\text{Pa}/^{235}\text{U}$ chronometer.

2.6 THERMOGRAVIMETRIC ANALYSIS IN COMBINATION WITH MICRO-RAMAN SPECTROSCOPY

The 8 UOC samples were analysed by thermogravimetric analysis (TGA) in both air and nitrogen atmospheres; the resulting profiles readily differentiated between UOCs of different species (i.e. U_3O_8 samples from Olympic Dam and Ranger, and $\text{UO}_4 \cdot n\text{H}_2\text{O}$ samples from Beverley) (Fig. 5) [2]. The moisture content was found to be the major difference between the U_3O_8 samples from Ranger and Olympic Dam, as the samples from Ranger lost between 1 – 1.5 % weight at 100 °C, whereas the samples from Olympic Dam lost only ~ 0.5 % weight. Thermal decomposition of the UO_4 samples from Beverley was consistent with the literature [4]. The species that underwent two separate decomposition processes within the Ranger and Olympic Dam profiles (at ~300 °C and ~610 °C) were unable to be identified.

Micro-Raman spectroscopy was a valuable analytical technique used to investigate the speciation of the UOCs, the TGA products and the different intermediates that formed following thermal decomposition at certain temperatures. In addition to U_3O_8 , UOCs from Ranger and Olympic Dam were found to contain UO_3 as a minor phase, which decomposed at ~ 300 °C to form an unidentified species which had a broad Raman band at ~ 687 cm^{-1} . With further heating, this species decomposed to form U_3O_8 . The μ Raman spectra obtained from the Beverley UOC set of samples were again consistent with the literature, however, upon decomposition of $UO_4 \cdot 2H_2O$ to amorphous- UO_3 (A- UO_3) at ~ 220 °C, two Raman bands appeared at 692 and 758 cm^{-1} in addition to the new UO_3 band at 839 cm^{-1} . Interestingly, upon heating the Beverley samples to 500 °C and forming α - UO_3 from A- UO_3 [4], the relative intensities of these two new Raman bands reversed. Upon heating further to 1000 °C, the two unknown Raman bands were no longer present as the α - UO_3 decomposed to form U_3O_8 . X-ray diffraction was performed to chart the decomposition of the Beverley, Ranger and Olympic Dam samples however it did not provide any additional information that could be used to elucidate the unknown species identified within the μ Raman spectra.

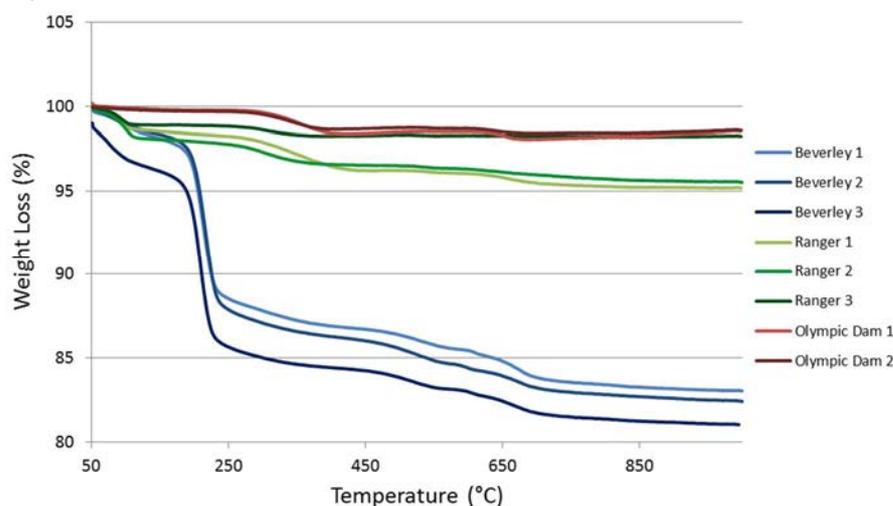


FIG 5. TGA profiles of Beverley, Ranger and Olympic Dam UOCs in an air atmosphere.

2.7 NEUTRON ACTIVATION ANALYSIS (NAA)

The rare earth elements (REE) are a highly valuable signature for identifying the provenance of UOCs, as the chondrite-normalised REE pattern of the UOC appears to be unaltered from that of uranium ore despite the series of metallurgical processes involved in the production of UOCs.

Neutron activation analysis (NAA) of the seven uranium ore samples was performed at the OPAL reactor at ANSTO, to characterise their trace and rare earth elemental composition. The REE data was used to compare the chondrite-normalised REE pattern of the uranium ores and their corresponding UOCs with values from the literature, to further explore the relationship between the two materials. In addition to the seven uranium ore samples, a number of uranium ore certified reference materials (OREAS 100a, 106, 120 and 124) were analysed to enable evaluation of NAA for this material type.

The experimental results of the OREAS analysis mostly agreed with the certified values, with the exception of a number of REE which were not detected or found to be present at higher concentrations due to interferences arising from the fission of uranium present within the sample. For example, in a neutron activated sample ^{153}Sm can be produced both as a fission product of ^{235}U as well as from the activation of samarium. While corrections can be applied to differentiate how much ^{153}Sm originated from the activation of samarium and how much from the fission of uranium, at high levels of uranium such corrections are ineffective. The chondrite-normalised REE patterns of the Australian UOCs and their respective uranium ores agreed where a comparison could be made, with the exception of the Ranger ore samples as the REE pattern has been shown to change according to the percentage of uranium

within the mineralisation [5]. These results support the conclusions made previously between the retention of the chondrite-normalised rare earth patterns through the UOC production process, but highlight the care needed during the interpretation of the results concerning the assignment of an ore samples as being 'representative' of an entire deposit.

3. CONCLUSIONS

Australia is actively working on the development of high confidence nuclear forensic signatures, particularly in the area of uranium ores and UOCs. Of the techniques investigated here, SEM offers one of the most promising areas of future research. Future work on UOCs may also include application of synchrotron techniques such as small angle X ray spectroscopy (SAXS) to investigate if it is possible to establish quantitative measures of the morphological differences between UOC samples from different locations. Synchrotron X ray fluorescence microscopy (XFM) to examine the spatial distribution of rare earth (REEs) and trace elements within individual grains of UOC may also be of interest.

Plans have been made to investigate the potential for ANSTO's newly commissioned 1 MV accelerator system, named VEGA, which was custom designed with the capability to perform high efficiency, high precision actinide mass spectrometry, to measure $^{231}\text{Pa}/^{233}\text{Pa}$ isotopic ratios.

ACKNOWLEDGEMENTS

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IDENTIFICATION OF NUCLEAR FORENSICS SIGNATURES IN ENVIRONMENTAL SAMPLES

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1. INTRODUCTION

Environmental sampling within nuclear facilities and in surrounding areas has been used routinely by the IAEA for safeguards purposes since 1996 [1, 2]. More recently, it has been suggested for use in the nuclear forensic field as a non-intrusive strategy that may be able to identify undeclared nuclear activities [1, 3].

The programme aims for the improvement of classical approaches for sampling and analysis of environmental samples and to evaluate new strategies for the application of these methodologies to include nuclear forensics.

2. WORK CONDUCTED

The Nuclear Fuel Department (CCN) at the Nuclear and Energy Research Institute (IPEN), São Paulo, Brazil was used as a case study. CCN produces 20%-enriched U_3Si_2 -Al dispersion fuel for the IPEN nuclear research reactor IEA-R1. Environmental swipe samples (taken using common 10cm² cotton swipes) were collected inside and outside of the installation. Initially, traditional procedures of bulk analysis (with total digestion of the samples) were performed and nuclear signatures were identified in all analysed samples. A new methodology was evaluated that involved leaching the samples in 0.29 mol kg⁻¹ HNO₃ and immersion in an ultra-sound bath for 15 minutes. This methodology presented results of high quality with the advantage of requiring less chemical processing. Considering, in case of an actual investigation, sometimes, that samples have to be collected from difficult locations and with no possibility of re-sampling, a question for the research was how to improve the methodology avoiding the collection of a non-representative sample.

In order to address this question, a preliminary evaluation (in field) concerning the amount of uranium present in the collected sample is calculated using a theoretical equation described by Rucker [4] which correlates the uranium specific activity (μ Ci/g of uranium) versus enrichment. It is assumed that the total alpha activity measured in the cotton swipe (in our case measured in Bq) is only due to uranium, and in this case, based on the declaration of the operator that the installation uses uranium enriched up to 20% in ²³⁵U.

After sample collection the next challenge is how to extract the maximal information from the swipe material. So, the new protocol starts with analysing the material by scanning electron microscopy with energy dispersive X ray spectroscopy (SEM-EDX) in order to identify particles, their morphology, the presence of uranium, its chemical form as well as major impurities.

Two techniques have been used to analyse the collected samples for bulk analysis: inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The results obtained with ICP-MS presents less uncertainty in the results than LA-ICP-MS. On the other hand, the latter technique allows one to select the region to be analysed from the surface of the cotton and, in some cases, when it is possible to identify a higher number of particles, provides better results. In both cases the results are strongly influenced by the environment. Samples collected in the most inner part of the installation have less influence owing to the uranium naturally present in the environment (considering that we also collect samples on the floor and walls

inside and outside of the installation). Efforts are still in progress with the objective to evaluate the possibility to analyse – individually - particles found in the samples.

In the future, further infrastructure will be included for a larger scale sampling plan based on remote sensing technologies.

The objective of the remote sensing work is to address three basic questions: where is the optimal site to collect the samples (related to the wind dispersion), which is the best biomonitor to be used (related to the ground environment) and, finally, what is the best design of the sampling procedure (related to the procedures and area where sample collection will be performed).

For this purpose, two systems are to be evaluated. The first one, already in place, is a SODAR (Sonic Detection and Ranging) system. The second one is a Doppler LIDAR (Light Detection and Ranging) which is currently being acquired. Both techniques employ the Doppler effect to detect the movement of air within the atmospheric boundary layer (ABL) and to infer wind speed and direction. In the case of LIDAR, electromagnetic radiation is reflected off particles, whereas with SODAR, a pulse of sound is reflected off the varying temperature structure in the atmosphere. The obtained data will be used as input for dispersion models and to define the sampling conditions. This scheme is illustrated in Fig 1.

Once collected, the samples will be transported to IPEN for detection of nuclear signatures using the infrastructure of the Brazilian Network Laboratories on Nuclear Forensics.

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IDENTIFICATION OF NUCLEAR FORENSIC SIGNATURES IN ENVIRONMENTAL SAMPLES**

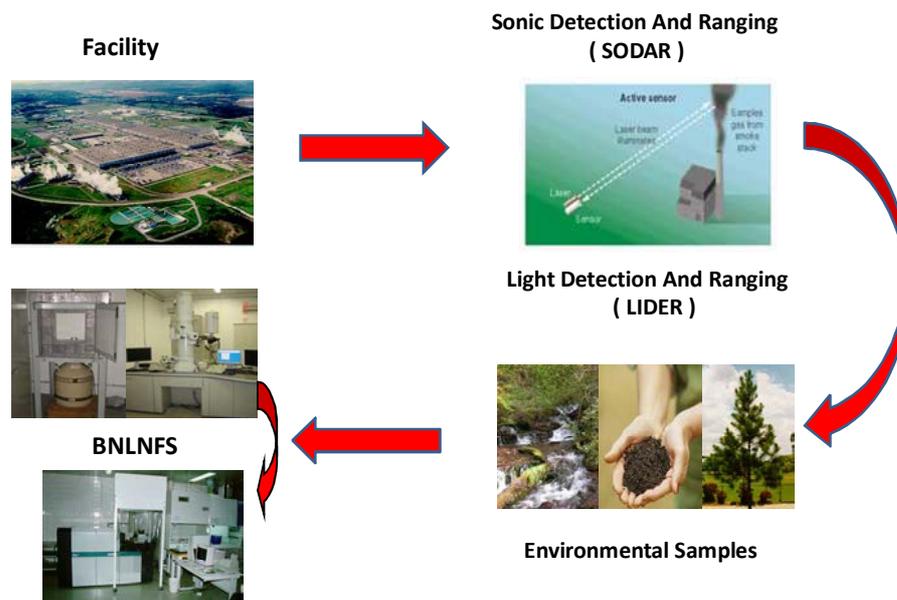


FIG 1. Scheme for identification of nuclear forensics signatures in environmental samples.

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NUCLEAR FORENSICS SIGNATURES OF IRRADIATED CANDU FUEL

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1. INTRODUCTION

Canada recognizes that an essential component of our national nuclear forensics capability is the development of a National Nuclear Forensics Library (NNFL). As part of the Canadian National Nuclear Forensics Capability Project, funded by the Canadian Safety and Security Program (administered by Defence Research and Development Canada), a prototype NNFL was developed under the leadership of the Canadian Nuclear Safety Commission. The primary focus of the NNFL was uranium ore concentrates. Given the unique expertise and access to data, the Canadian Nuclear Laboratories (CNL, formerly Atomic Energy of Canada Ltd.) is contributing to the national effort to develop the NNFL by conducting research into identifying potential signatures of irradiated CANDU[®] fuels.

2. WORK CONDUCTED

As part of Canada's nuclear fuel development programme, testing of experimental and prototypical fuels has been on-going for decades at the Chalk River site. This programme of fuel testing and performance assessments, including post-irradiation examination (PIE), has accumulated a considerable amount of information on irradiated fuels of different types, including uranium-based, mixed-oxide (MOX), and thoria-based fuels. The objective of the research is to determine potential signature models of irradiated CANDU fuels. These models will be based on correlations of isotopic composition and fission product contents of irradiated fuels obtained from reactor physics code calculations, validated with actual measured data obtained from PIE.

The methodology adopted for this research involves the development of validated correlations of specific isotopic ratios and fission product inventories as a function of power and burn-up, to determine any unique trends that can potentially differentiate these fuels from other fuels irradiated in other reactor types. Initial efforts have been focused on MOX fuels irradiated in the National Research Universal (NRU) research reactor. Several publications discuss isotopic correlations useful in determining the reactor type that the nuclear material originated from [1-6]. Most correlations are based predominantly on U and Pu isotopic data. One example of a list of isotopic correlations that can help identify potential signatures of irradiated fuel is shown in Table 1 [7].

TABLE 1. ISOTOPIC CORRELATIONS USEFUL IN IDENTIFYING POTENTIAL SOURCES OF INTERDICTED IRRADIATED FUEL (USED BY CNL DURING THE “GALAXY SERPENT” TABLE-TOP EXERCISE) [7]

Burn-up verses $^{235}\text{U}/\text{Total U}\%$	$^{240}\text{Pu}/^{239}\text{Pu}$ verses $^{235}\text{U}/\text{Total U}(\%)$
$^{234}\text{U}/\text{Total U}$ verses $^{235}\text{U}/\text{Total U}(\%)$	$^{240}\text{Pu}/^{239}\text{Pu}$ verses Burn-up
$^{236}\text{U}/\text{Total U}$ verses $^{234}\text{U}/\text{Total U}(\%)$	$(^{241}\text{Am}+^{241}\text{Pu})/^{239}\text{Pu}$ verses Burn-up (^{148}Nd)
$^{234}\text{U}/\text{Total U}$ verses $^{236}\text{U}/\text{Total U}(\%)$	$^{242}\text{Pu}/^{240}\text{Pu}$ verses $^{235}\text{U}/\text{Total U}(\%)$
Total Pu/ ^{238}U verses $^{235}\text{U}/\text{Total U}(\%)$	$^{242}\text{Pu}/^{238}\text{Pu}$ verses $^{240}\text{Pu}/^{239}\text{Pu}$
$^{239}\text{Pu}/^{238}\text{U}$ verses Burn-up (^{148}Nd)	$^{99}\text{Tc}/^{137}\text{Cs}$ verses Burn-up (^{148}Nd)
$^{238}\text{Pu}/^{238}\text{U}$ verses Burn-up (^{148}Nd)	$^{241}\text{Pu}/^{240}\text{Pu}$ verses $^{235}\text{U}/\text{Total U}(\%)$

Four major experiments involving different MOX fuels were identified as having adequate PIE data with sufficient detail in terms of U and Pu isotopic composition. As seen in Table 2, these experiments involved a wide variety of Pu content, Pu isotopic composition, matrix materials, and a range of powers and burn-ups. The amounts of actinides and fission products produced during irradiation in these experiments under representative NRU reactor conditions were calculated using the WOBI (WIMS-ORIGEN Burn-up Integration) code. To validate the WOBI results, these calculated values were compared to chemically measured values from PIE.

TABLE 2. MOX FUEL EXPERIMENTS USED TO DETERMINE POTENTIAL SIGNATURES

Experiment Number	Pu Content (wt% in HE)	Pu Isotopic Type	Matrix Material	Burn-up (MWd/kgHE)
BDL-419	0.50	Reactor-grade	Natural U	Up to 35
BDL-441	3.1	Weapons-grade	Depleted U (0.3 wt% U-235)	Up to 17
BDL-446	1.35	Reactor-grade	Depleted U (0.37 wt% U-235)	Up to 22
BDL-447	4.6	Weapons-grade	Depleted U (0.3 wt% U-235)	Up to 10
BDL-447	5.3	Reactor-grade	Depleted U (0.3 wt% U-235)	Up to 10

The comparison between calculated and measured amounts of actinides was done using arbitrarily chosen ratios, mainly in an effort to minimize the effects of measurement and calculation uncertainties. As shown in Figures 1 – 6, the agreement between calculated and measured ratios is generally good, with some notable exceptions. It appears that MOX fuels containing higher amounts of Pu exhibit a slightly higher discrepancy between calculated and measured isotopic ratios. This observation indicates that when isotopic ratio correlations are being explored to determine potential signatures, care has to be taken to use only those ratios whose calculated and measured values have reasonable agreement.

Several isotopic ratios were correlated with burn-up to determine potential distinctive trends. As seen in Figure 7, the effect of the initial Pu content is clearly distinctive when $^{235}\text{U}/^{238}\text{U}$ ratio is plotted against burn-up. This correlation also shows that one is able to back extrapolate the original ^{235}U enrichment of the uranium matrix material regardless of the initial Pu content. In Fig. 8, the $^{236}\text{U}/^{238}\text{U}$ ratio plotted against burn-up is significantly affected by the initial Pu content. This is because neutron capture in ^{235}U (which creates ^{236}U) depends on neutron flux. More fissile plutonium at the same power decreases neutron flux and ^{236}U production. However, at certain Pu contents, this effect seems to decrease. Fig. 9 shows the correlation of the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio against burn-up. The effects of both the initial Pu content and the isotopic composition of the Pu are clearly distinctive. At zero burn-up, one can see the difference in isotopic composition of the Pu. It is also worth noting that in some cases, a saw-tooth trend is seen. These changes in isotopic ratios with no increase in burn-up represent the effect of decay of short-lived isotopes resulting from pauses in the irradiation during the experiments when the fuel was removed from the core. Figs. 10 and 11 demonstrate the different trend lines when either the $^{241}\text{Pu}/^{239}\text{Pu}$ or the $^{242}\text{Pu}/^{239}\text{Pu}$ ratio is correlated with burn-up. The long vertical line segments in Fig. 10 indicate decay of ^{241}Pu after irradiation.

By elucidating mechanisms and validating the WOBI methodology and the underlying physics data, applications to uranium-based fuel can be justified. Higher burn-up CANDU fuel will see many of the nuclear reactions that occur in uranium/plutonium MOX fuel.

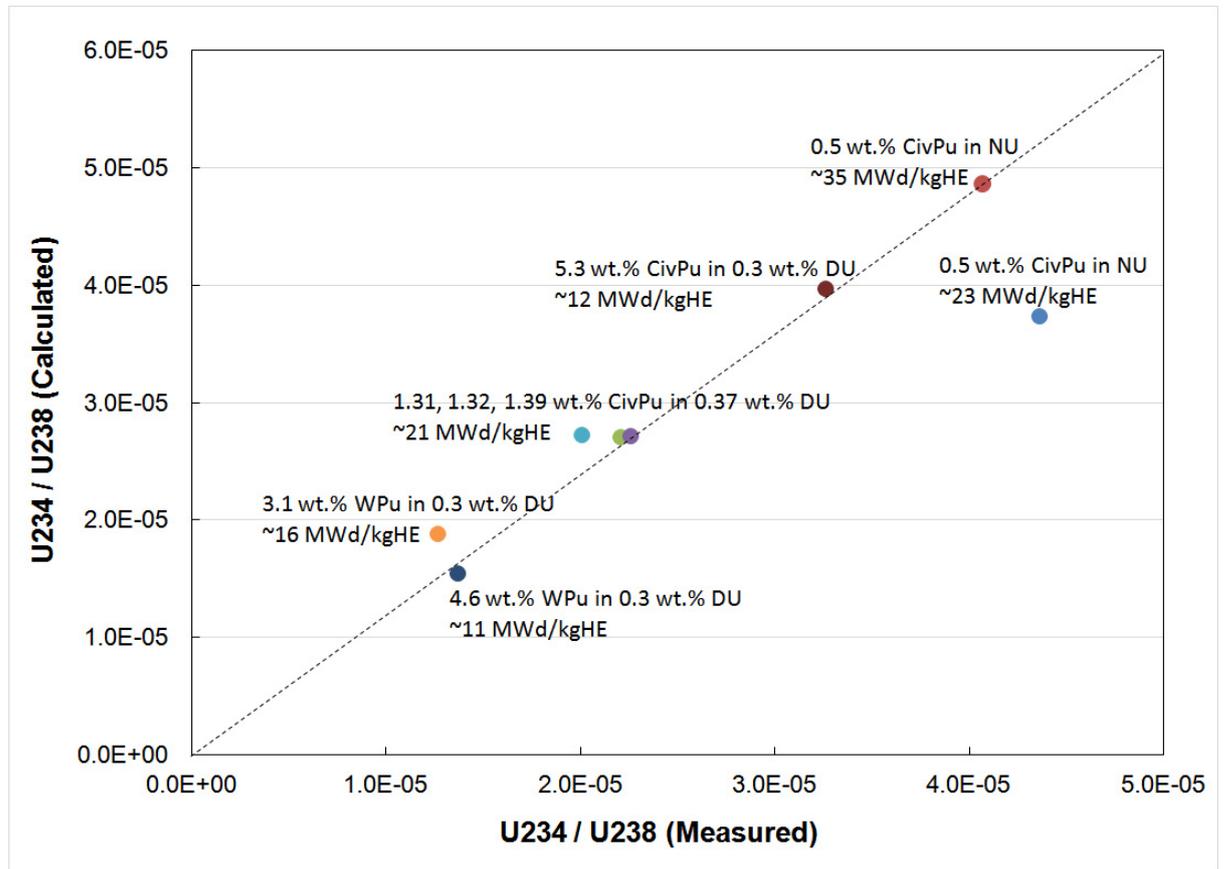


FIG 1. Comparison between measured and calculated values of $^{234}\text{U}/^{238}\text{U}$ ratio.

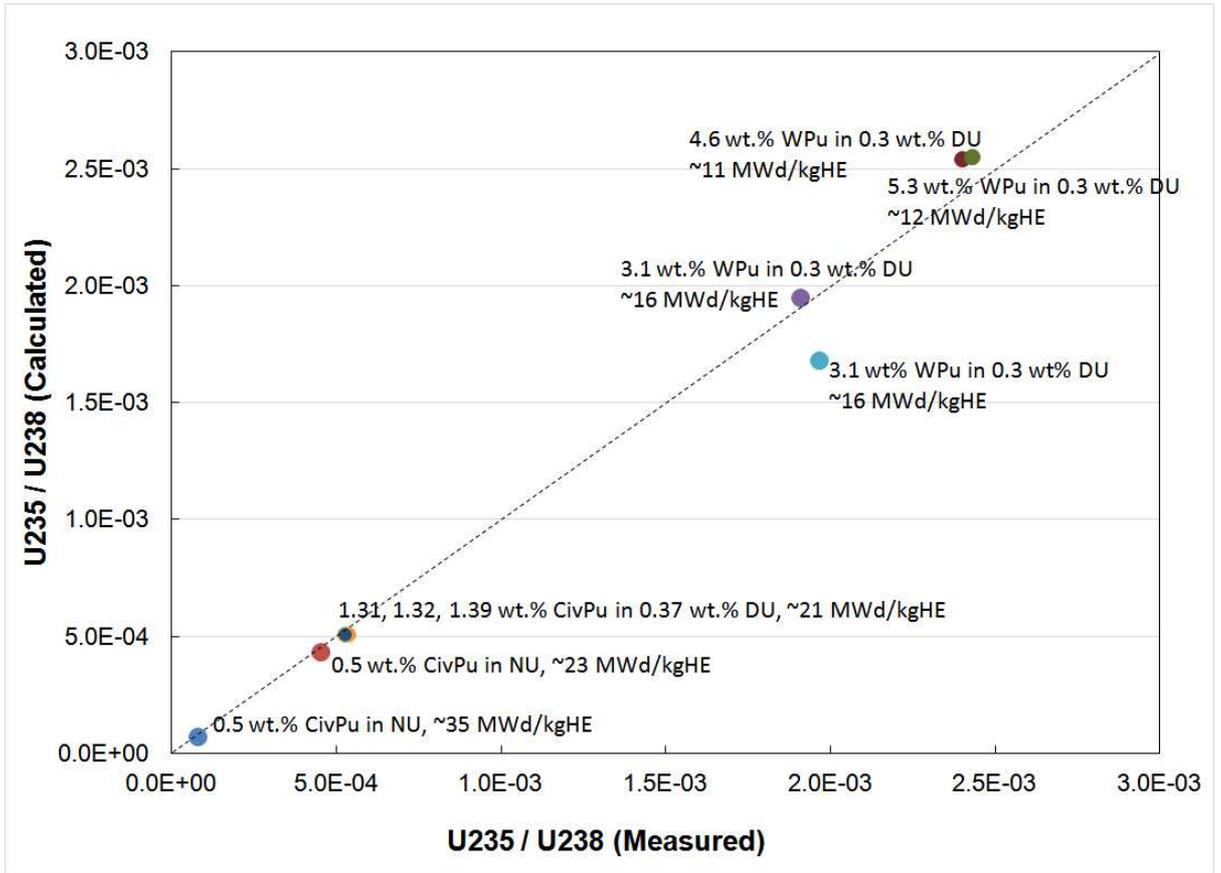


FIG 2. Comparison between measured and calculated values of $^{235}U/^{238}U$ ratio.

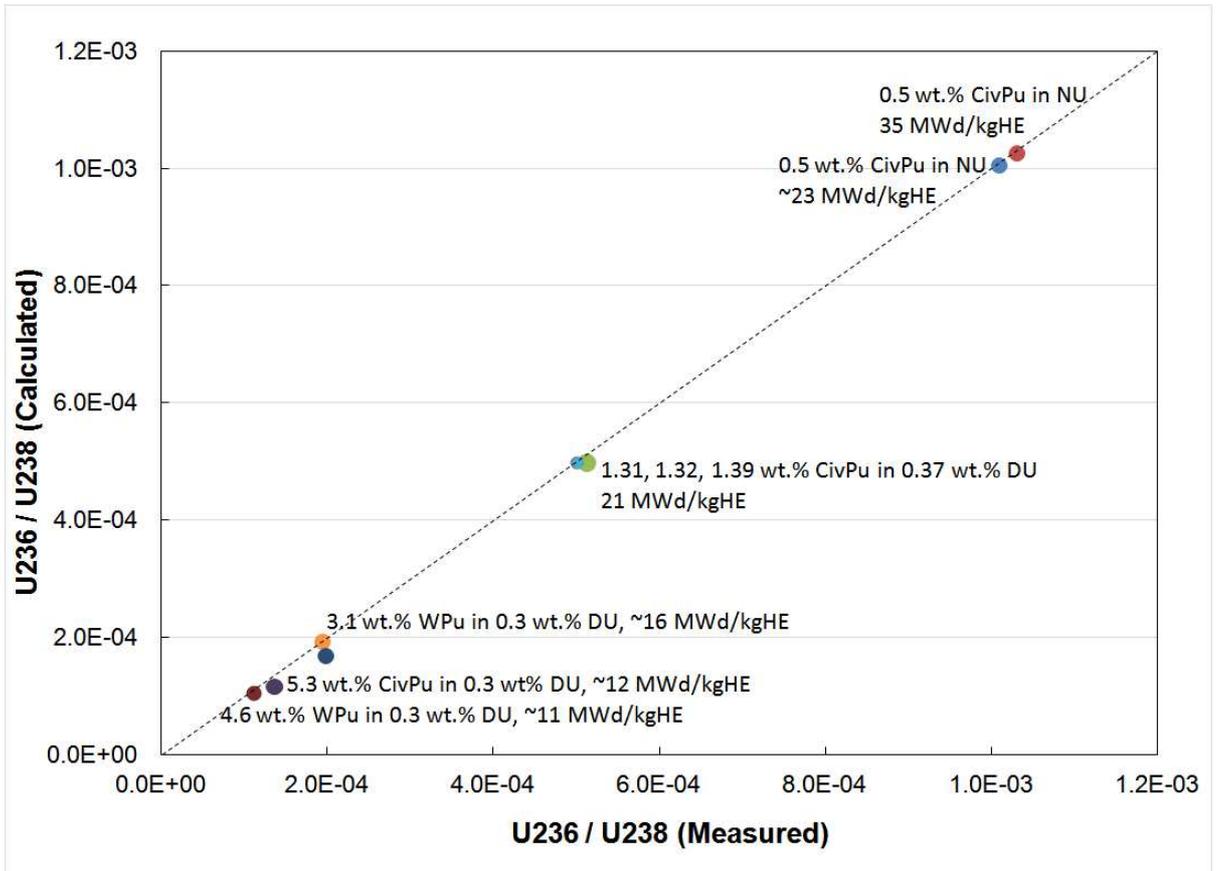


FIG 3. Comparison between measured and calculated values of $^{236}\text{U}/^{238}\text{U}$ ratio.

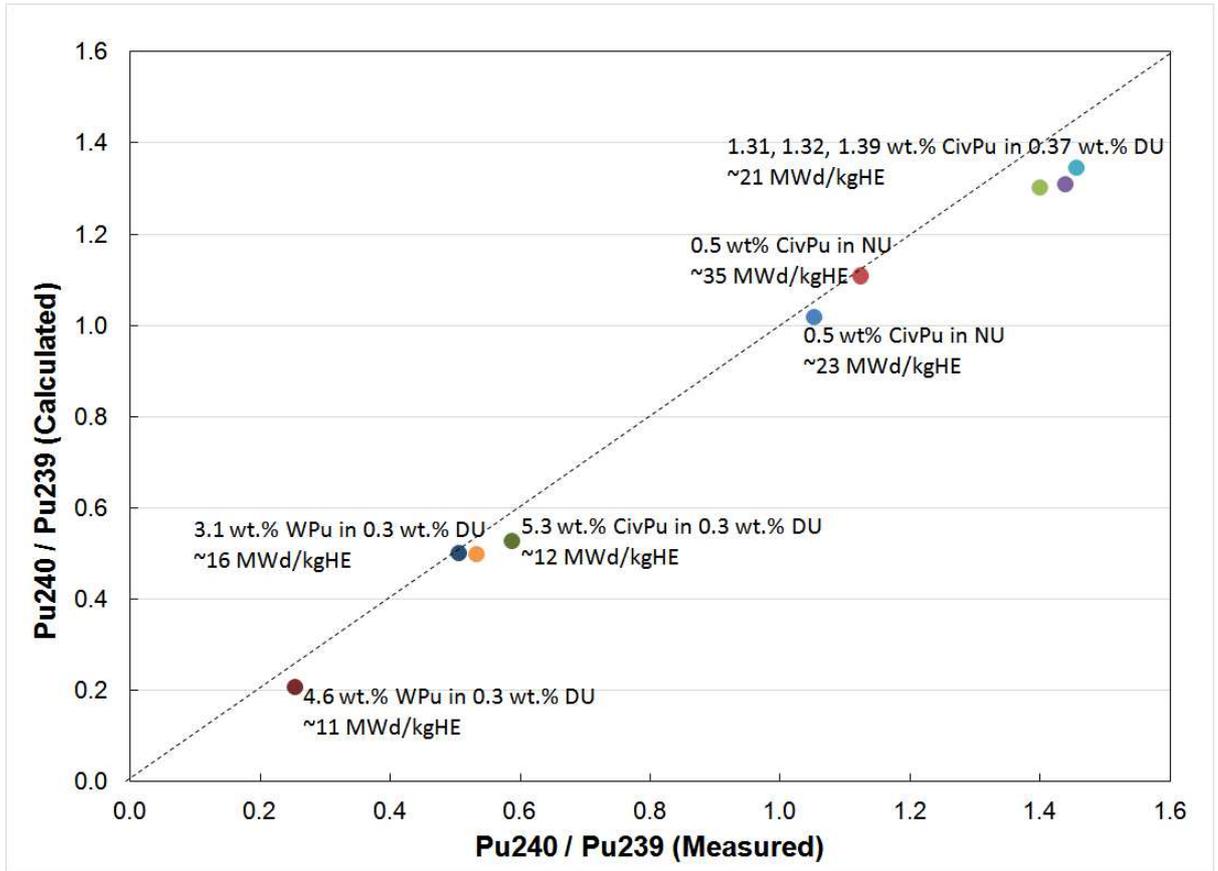


FIG 4. Comparison between measured and calculated values of $^{240}\text{Pu}/^{239}\text{Pu}$ ratio.

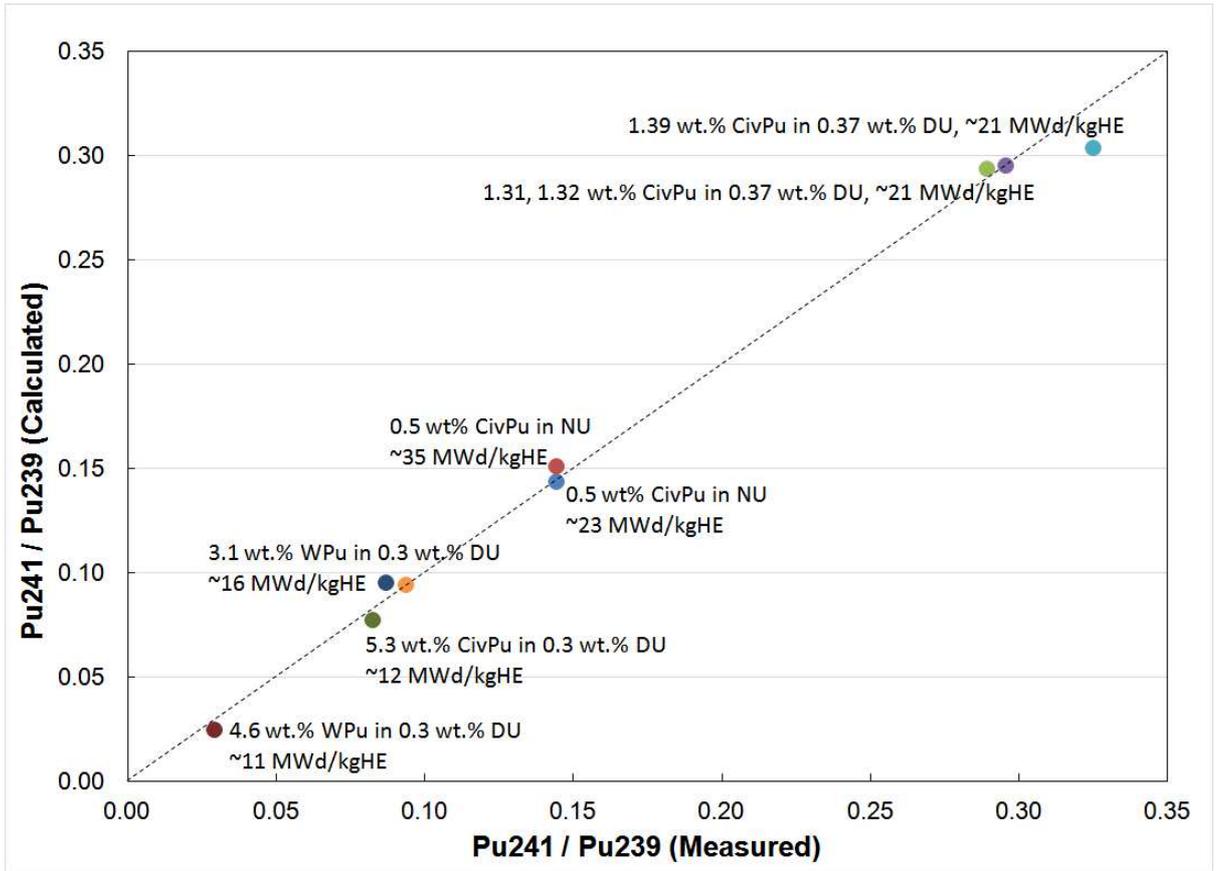


FIG 5. Comparison between measured and calculated values of $^{241}\text{Pu}/^{239}\text{Pu}$ ratio.

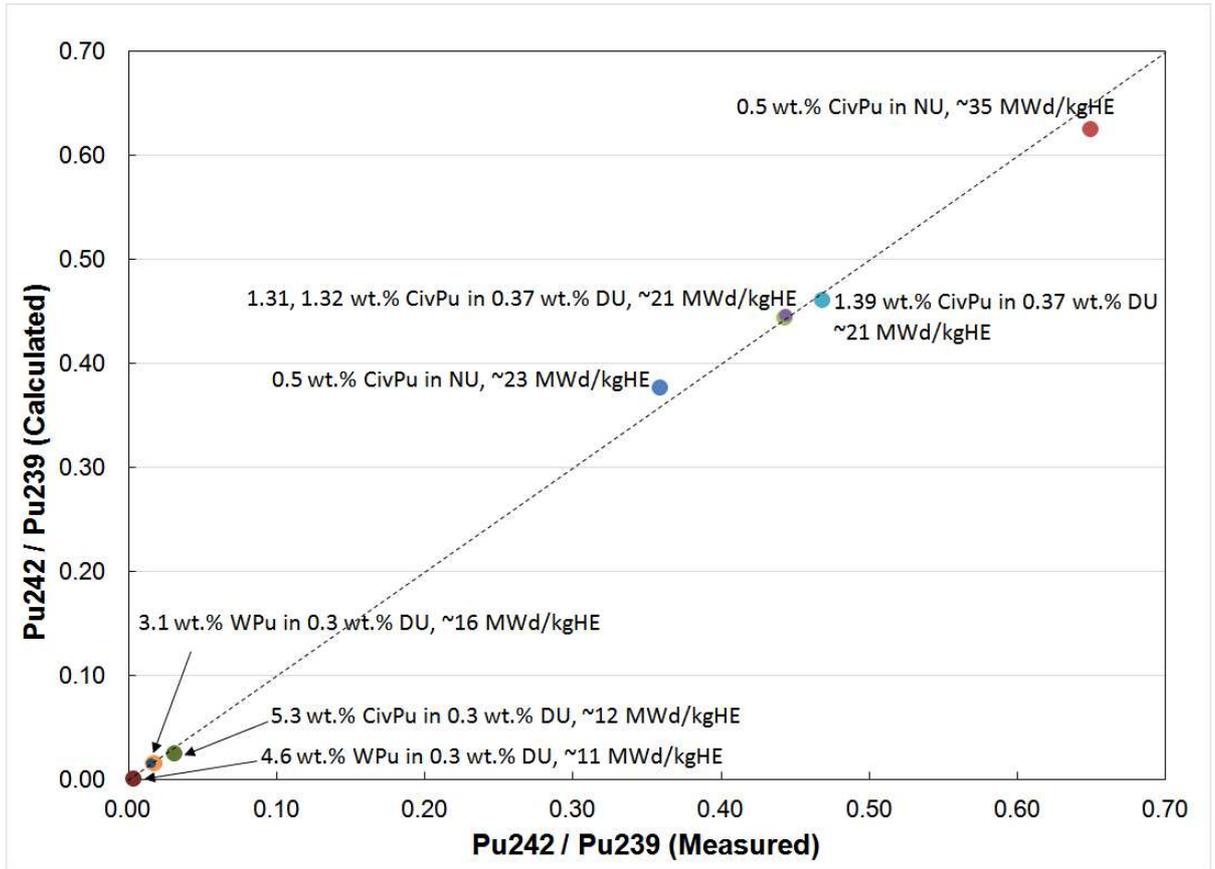


FIG 6. Comparison between measured and calculated values of $^{242}\text{Pu}/^{239}\text{Pu}$ ratio.

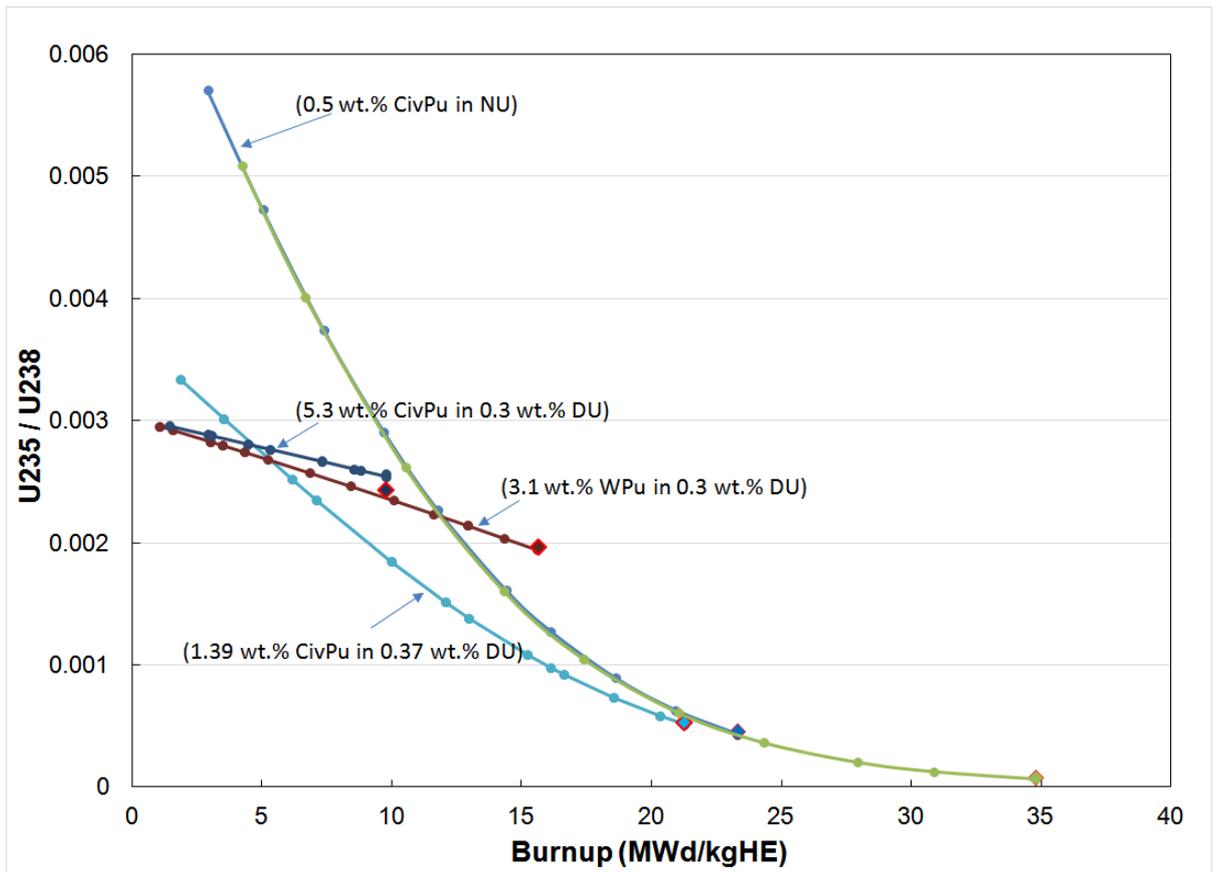


FIG 7. Correlation of $^{235}\text{U}/^{238}\text{U}$ ratio against burn-up.

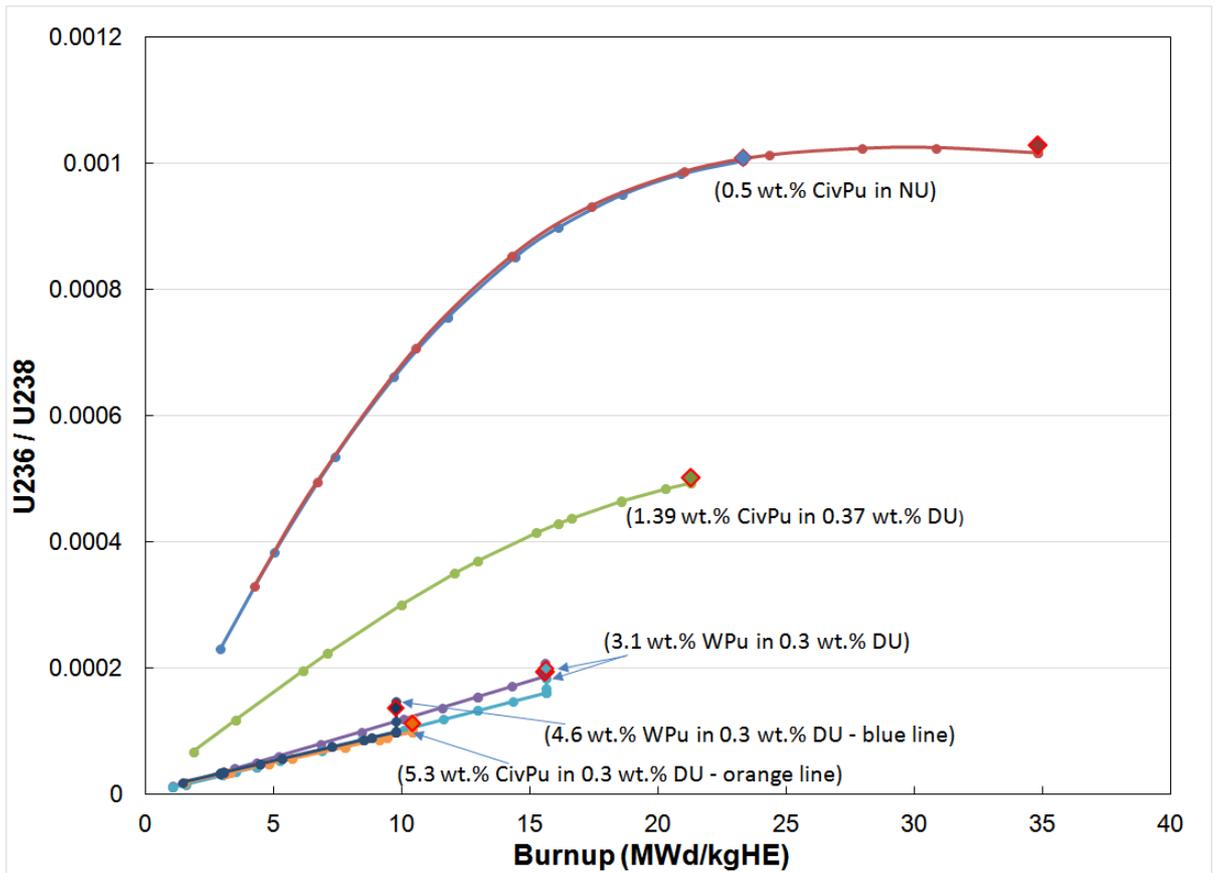


FIG 8. Correlation of $^{236}\text{U}/^{238}\text{U}$ ratio against burn-up.

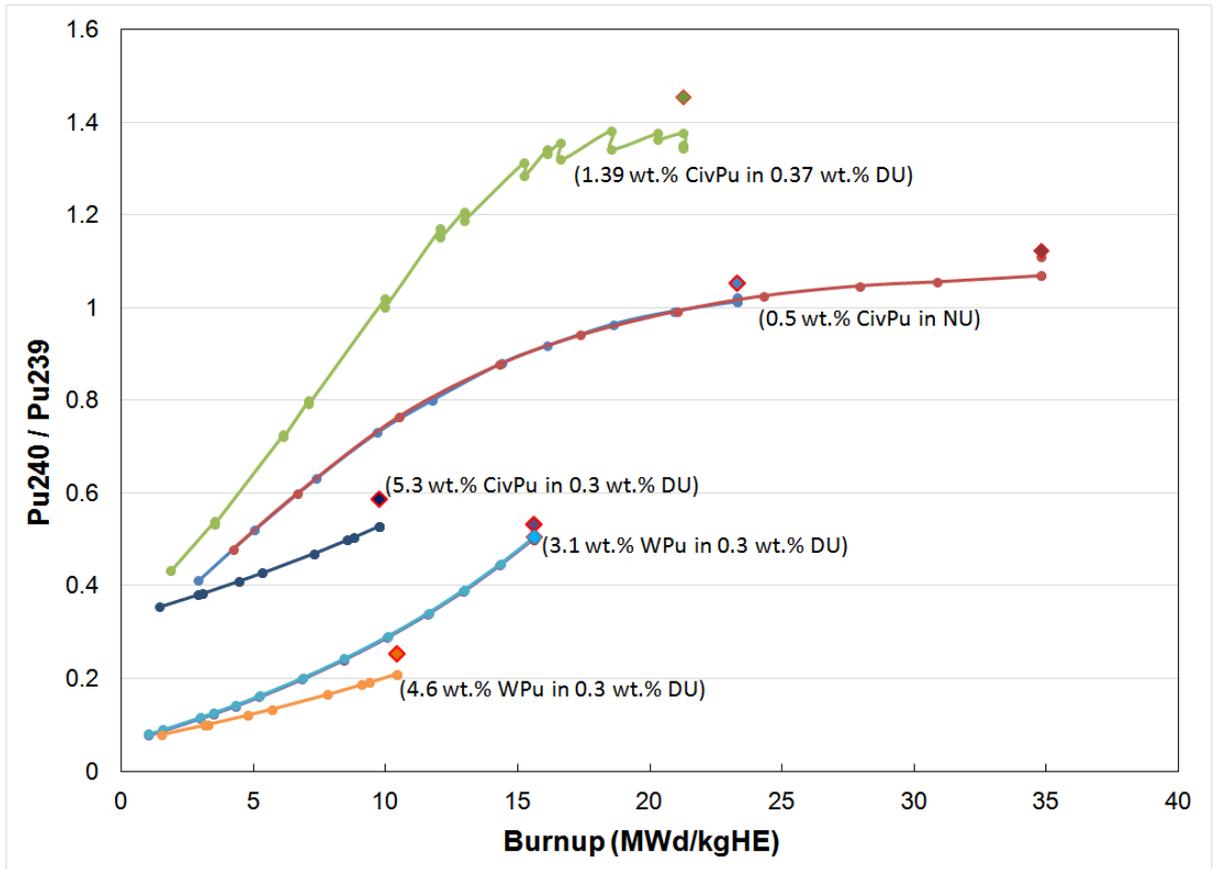


FIG 9. Correlation of $^{240}\text{Pu}/^{239}\text{Pu}$ ratio against burn-up.

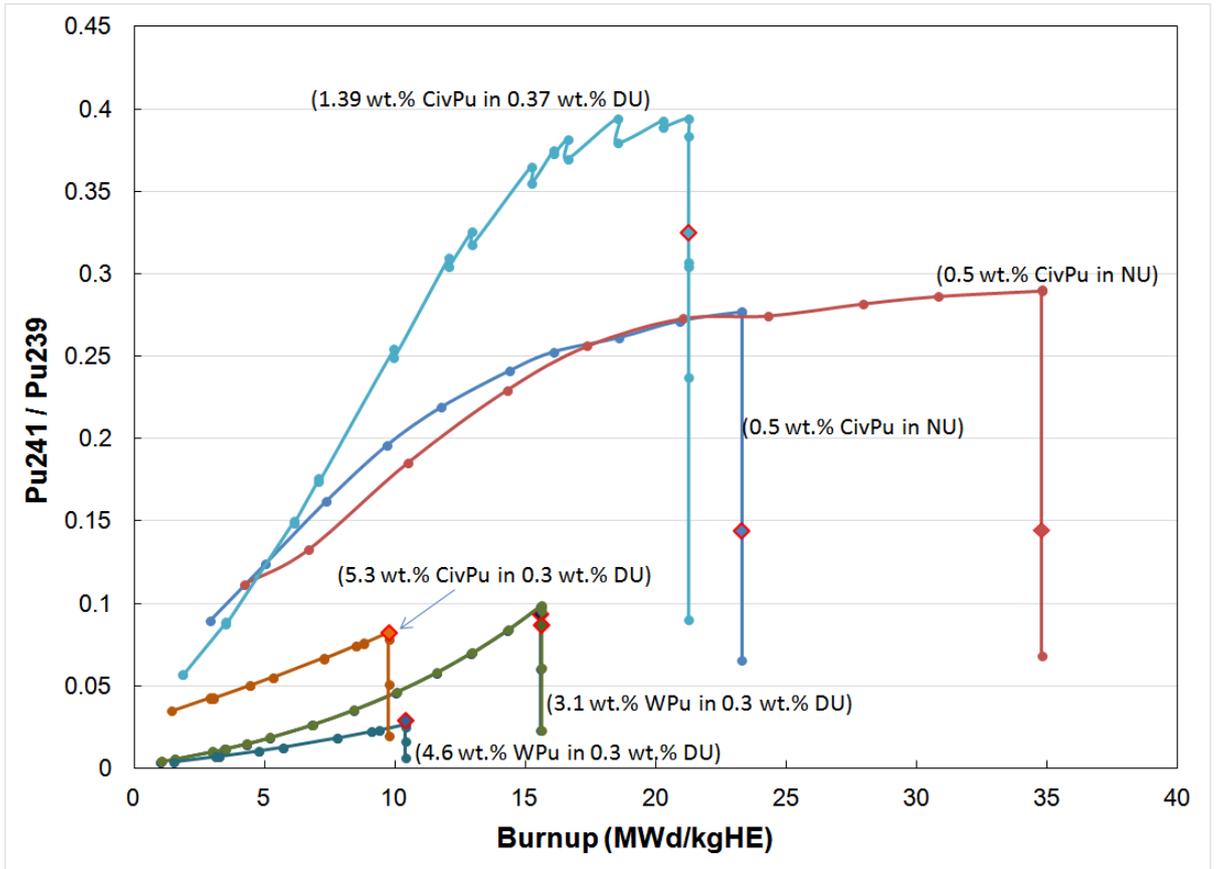


FIG 10. Correlation of $^{241}\text{Pu}/^{239}\text{Pu}$ ratio against burn-up.

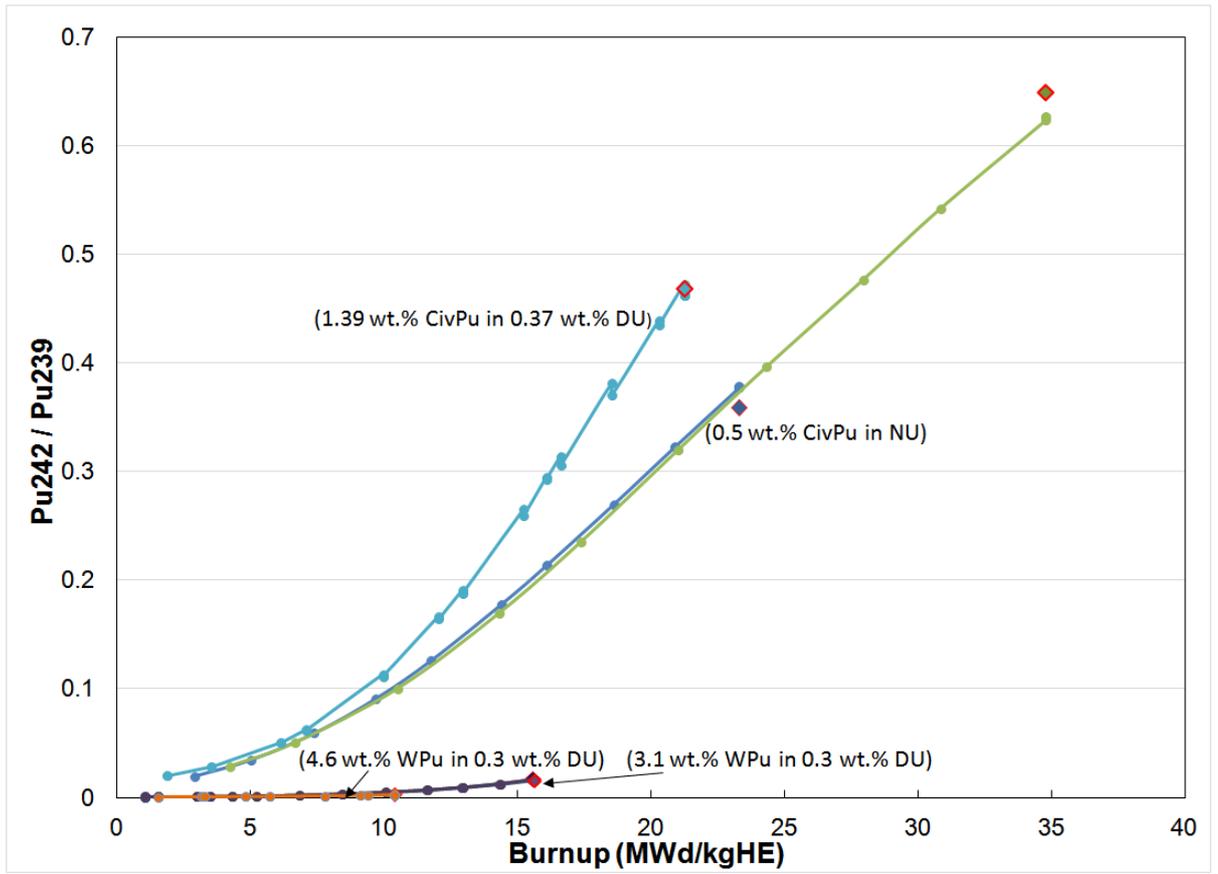


FIG 11. Correlation of $^{242}\text{Pu}/^{239}\text{Pu}$ ratio against burn-up.

3. CONCLUSIONS

To contribute to Canada's national effort to develop a national nuclear forensics library, CNL is conducting research into identifying potential signatures of irradiated CANDU fuels. The methodology employed for this research involves the identification of fuel data, particularly in terms of isotopic compositions and fission product analysis, from previous irradiation experiments. Reactor physics calculations are performed to determine the theoretical isotopic ratios and fission product contents, which are then compared to measured values. Results of this comparison indicate that not all isotopic ratios are useful for the development of these correlations. Possible reasons for some of the discrepancies between measured and calculated values include experimental errors in the measurements as well as modelling uncertainties in conducting the WOBI calculations. Based on these observations, the use of isotopic correlations for attribution should be done with care and diligence to avoid misleading conclusions. However, it is also evident that correlations of specific isotopic ratios can be employed to determine unique trends that can potentially differentiate these fuels from others irradiated in other reactor types.

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PROPAGATION OF NUCLEAR FORENSICS SIGNATURES AT THE FRONT-END OF THE FUEL CYCLE

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1. INTRODUCTION

An earlier IAEA Coordinated Research Project study undertaken by the European Commission on "Procedures and Techniques for Nuclear Forensics Investigations" examined various potential signatures (e.g. metallic and anionic impurities, Pb and Sr isotope ratios, U minor isotopes) in a large suite of uranium ore concentrate (UOC) samples [1]. The results of that study clearly identified several signatures, to include rare earth element (REE) patterns and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which can be exploited to provide information on the type of uranium ore deposit, and therefore, on its geolocation. However, in order to explore if these identified signatures have the potential to be further used in more processed U-compounds, it is necessary to study their robustness through further (chemical) processing and to examine if they propagate without alteration into uranium products such as UO_3 , UO_2 and UF_4 . In order to understand stability or alteration of signatures, the accompanying chemical and technological processes have to be considered. The present CRP study "Propagation of Nuclear Forensics Signatures at the Front-End of the Fuel Cycle" addresses this issue. In addition, new isotopic signatures have been studied.

2. WORK CONDUCTED

2.1 SAMPLES AND PROCESSES

Samples originating from four industrial facilities of two different countries were analysed in the study (Table 1). In addition, selected UOCs (a batch of total 79 samples, used also in the earlier CRP study) were analysed for new signatures.

TABLE 1. NEW SAMPLES INVESTIGATED IN THE PRESENT CRP STUDY AND THE RESPECTIVE PROCESSES (COUNTRY AND FACILITY NAMES INTENTIONALLY ANONYMIZED).

Country	Facility	Process	Number and type of samples
S	SU	Uranium ore → ammonium diuranate (ADU)	Ore powder, ADU slurry, 5 liquid samples from various process stages (e.g. leachate, ion exchange eluate)
S	NU	ADU → U_3O_8	ADU slurry, ADU powder, U_3O_8 powder
C	BR	UOC → UO_3	16 UOCs (from 4 different mills), 6 UO_3 , 16 process stage samples and chemicals
C	PH	UO_3 → UF_6	5 UO_3 , 2 UO_2 , 8 UF_4 , 3 UO_2F_2 , 3 process reagents

2.2 RESULTS

2.2.1 Elemental impurities

All the samples were analysed for impurities by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS). Following are the main conclusions obtained from the analysis of the samples from different processes:

Uranium ore → ADU → U_3O_8

- Sulphuric acid leaching of the U ore highly and selectively affects the rare earth element (REE) impurity pattern;
- Following ion exchange and solvent extraction processes that effectively remove most of the impurities only some elements (e.g. Mo, Zr), that form anion complexes, are retained that are (relatively) unchanged;
- The REE pattern remains to a large extent unaltered (only the lighter REE pattern from total dissolution of the ore is slightly altered, Fig.1) and can be thus used as a robust signature for U-products coming even from the later stages of the front-end of the fuel cycle to give information about the U ore deposit type.

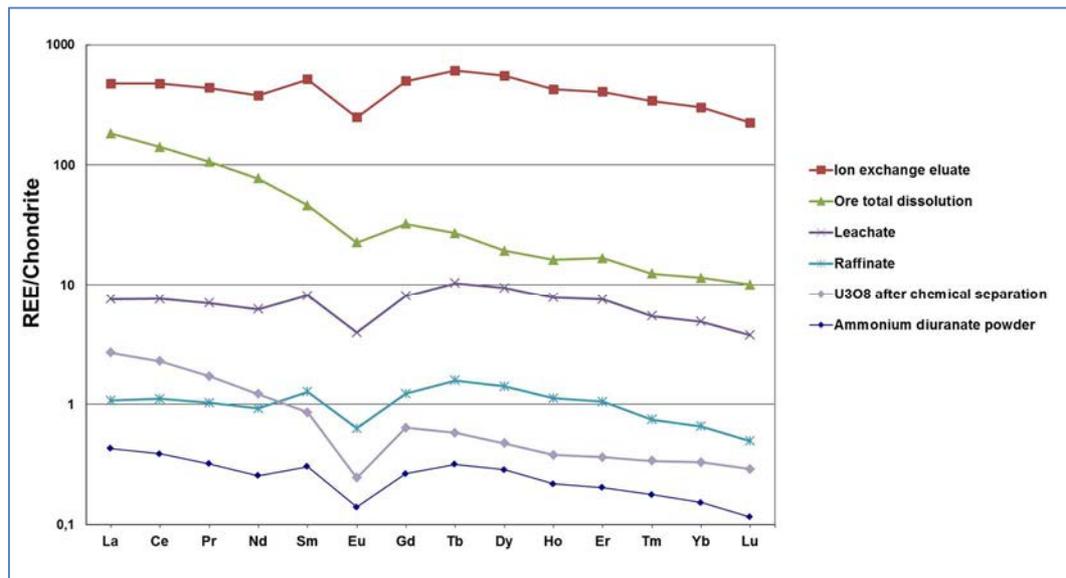


FIG.1. REE pattern in investigated samples from ore processed through U_3O_8 powder.

UOC → UO_3

- Variations (up to 85 %) in impurity content between UOC batches coming from the same mill (sampled at the same time) were observed;
- Digestion of the UOCs by nitric acid introduced impurities such as Co, Cr, and Fe in feed slurry. These originate very likely from the process piping. Also P content was increased by orders of magnitude as H_3PO_4 was used in the processing;
- Solvent extraction removed effectively most of the impurities and the final UO_3 product was very pure;
- The REE pattern seemed to remain unaltered.

UO₃ → UF₆

- Hydro-fluorination (i.e. HF used in a “wet process”) introduced large amount of impurities, the highest being B, Ca, Fe, S and Si;
- Calcination of the UF₄ removed some volatile elements completely, to include As and Pb;
- UF₆ production removed effectively the elements forming non-volatile fluorides, including Co, Na, Th and REE.

2.2.2 Age determination

U products from all four facilities were chosen and tested for age determination (Table 2). The process used in the facility SU in country S for producing ADU slurry effectively separated Th from the U and the resulting age determination using ²³⁰Th/²³⁴U chronometry gave correct results.

TABLE 2. RESULTS OF THE AGE DETERMINATION

Facility	Product	Measured age	Known age
S-SU	ADU Slurry	282 ± 56 days	307 days
S-NU	U ₃ O ₈	318 ± 74 days	305 days
C-BR	UO ₃	1.86 ± 0.03 years	1.0 years
C-BR	UO ₃	6.8 ± 0.1 years	1.0 years
C-PH	UF ₄	3.90 ± 0.03 years	1.3 years
C-PH	UF ₆ (UO ₂ F ₂)	1.20 ± 0.08 years	1.3 years

On the other hand, the process to produce UO₃ in another country and facility (C-BR) neither separated Th effectively nor in a reproducible way (difference between samples). Therefore, the obtained ages were biased. However, as the residual amount of Th was not excessive and the determined ages were still realistic (i.e., not on the order of 200 years old), the assumption can be made (if the production date was not known) that the determined ages are correct. For these reasons, the use of a second parent/daughter chronometer (e.g. ²³¹Pa/²³⁵U or ²²⁸Th/²³²Th) in parallel and a careful evaluation of the Th content is recommended.

The UO₃ starting materials for the samples converted to UF₆ in C-PH originate from the facility C-BR. As observed previously, Th is not entirely separated from the UO₃ and the residual Th is propagated through the UF₄ production. However, Th has been removed completely during the UF₆ production and the determined age corresponded well to the date of conversion of UF₄ to UF₆.

2.2.3 Isotopic impurities

2.2.3.1 Lead and strontium

Lead and strontium were identified in the earlier CRP study as reasonably robust nuclear forensic signatures for UOC samples. In the current study their propagation was investigated using the sample sets S-SU and S-NU. The results demonstrated that for both Pb and Sr, the processing affects significantly the original isotope ratios of the ore. The process chemicals appear to contain enough Pb and Sr as contaminants to dilute the "radiogenic" Pb and Sr with the "natural" Pb and Sr. It was clearly observed that the more the samples are processed, the closer the isotope ratios are to the natural one (Fig. 2).

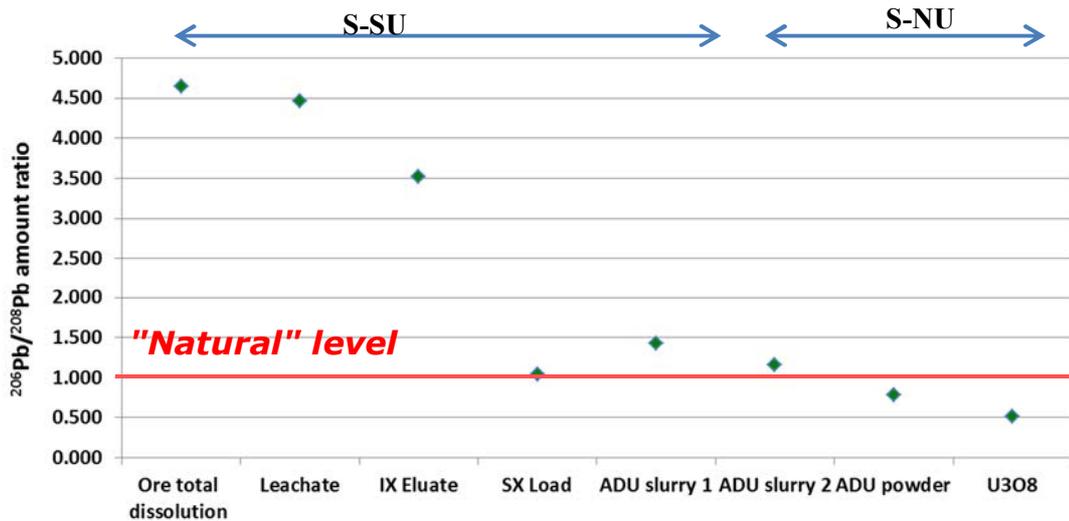


FIG 2. $^{206}\text{Pb}/^{208}\text{Pb}$ ratio in S-SU and S-NU samples.

2.2.3.2 Neodymium

Neodymium was investigated as a new nuclear forensic signature for the UOC samples. Nd, belonging to the group of rare earth elements, is expected to chemically follow uranium during the processing (similar to the other REE). Therefore, it is considered as being a good candidate for a nuclear forensic signature with less anticipated elemental fractionation (e.g. compared to Sr). Figure 3 shows the results of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio determination in selected UOCs. It was observed that the UOCs of certain type of deposits (e.g. intrusive, sandstone and quartz-pebble conglomerate) tend to show grouping of the ratio, whereas samples from other types of deposits do not exhibit this behavior (e.g. unconformity). Inhomogeneity in the ore body was detected as the ore samples and respective UOCs from two mines showed significantly different $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (as well as Sm/Nd ratios). However, these samples were not consecutive ore-UOC pairs, therefore the differences are not related to a change in the isotope ratio due to the processing.

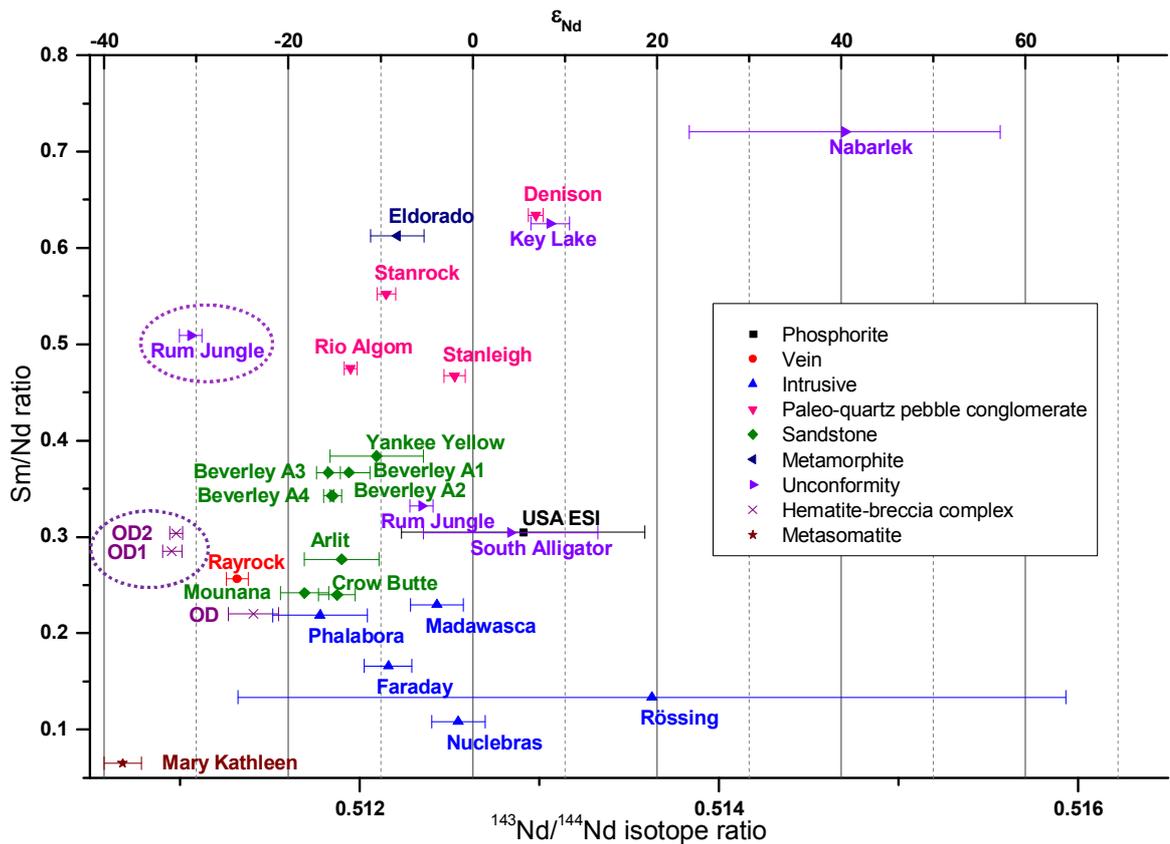


FIG.3. $^{143}\text{Nd}/^{144}\text{Nd}$ versus Sm/Nd in selected UOCs. Circled samples (OD1, OD2 and Rum Jungle) are U ores.

2.2.3.3 Sulphur

Sulphur was also investigated as a new signature in the UOC samples. As many sulphur containing reagents are used during UOC production (e.g. H_2SO_4 for uranium ore leaching), the $^{34}\text{S}/^{32}\text{S}$ ratio is expected to change and deviate from the original ratio of the ores. This was also observed in the leaching tests using various methods. The only case where the original $^{34}\text{S}/^{32}\text{S}$ ratio of the ores is preserved is in those UOCs samples where no sulphuric acid leaching is used. This case includes when carbonate agent based in-situ leaching is used (Fig.4, three samples on the left). The $^{34}\text{S}/^{32}\text{S}$ ratio propagation was tested for the S-SU and S-NU samples (Fig.5). In this case, after the solvent extraction, no additional S is added in the process and therefore the $\delta^{34}\text{S}$ remains similar in the further products (ADU and U_3O_8).

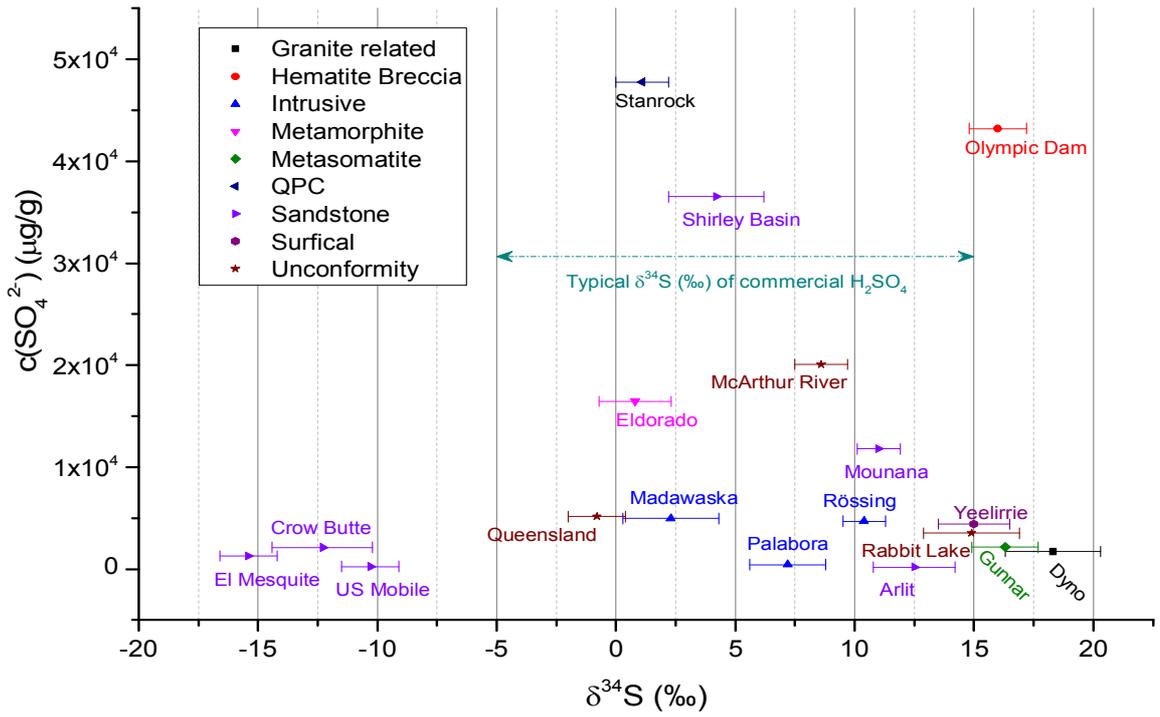


FIG. 4. $\delta^{34}\text{S}$ versus sulphate content in UOCs.

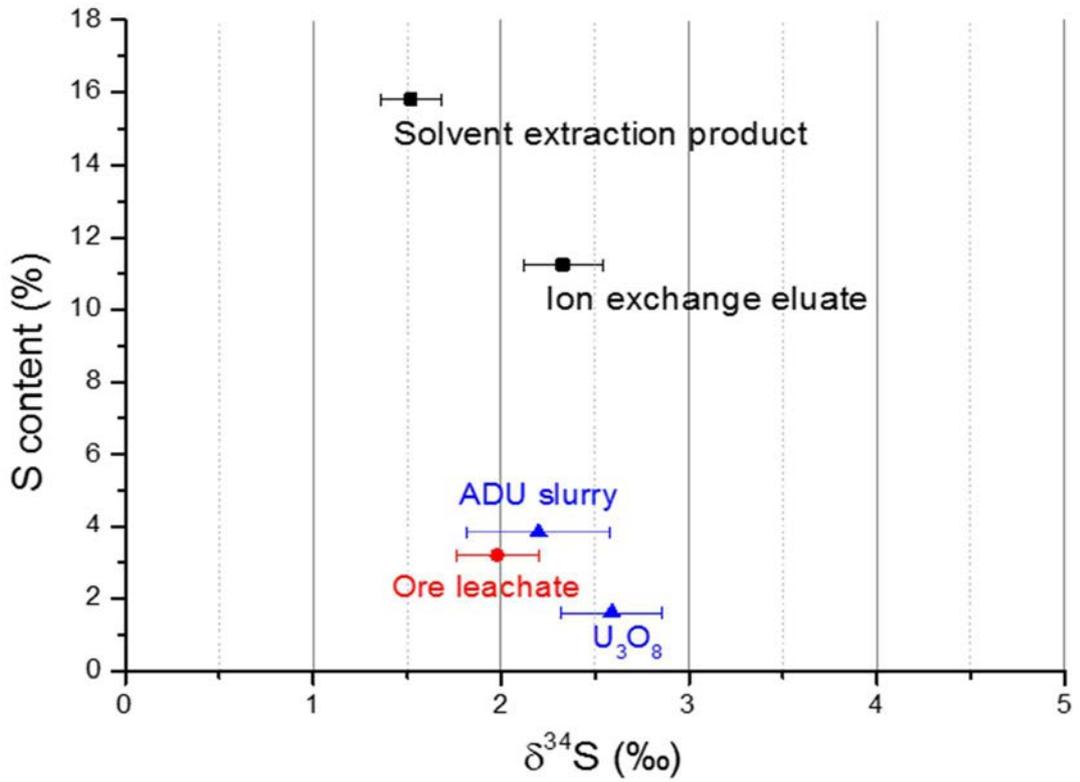


FIG. 5. $\delta^{34}\text{S}$ versus S content in S-SU and S-NU samples.

2.2.4 Morphology

Morphological studies (e.g. particle shape and size) were performed first for the industrial UOCs using scanning electron microscopy (SEM). When distinct differences were observed in the industrial samples, five common UOC compounds were synthesized in the laboratory in order to compare and explain the morphology: ammonium diuranate (ADU), sodium diuranate (SDU), uranium peroxide (UP), ammonium uranyl carbonate (AUC) and uranyl hydroxide (UH). Those compounds (i.e. ADU, SDU and UP), that could not be resolved from each other by SEM due to inadequate magnification were further investigated by transmission electron microscopy (TEM) which revealed differences in morphology.

Three of the synthesized UOCs (i.e. AUC, ADU and UP) were also studied to investigate if the calcination temperature has any effect on the morphology. It was observed that the temperature has no significant effect on the particle shape or size (Fig. 6). The morphology was studied for the S-NU samples and, again, no changes were observed. Therefore, it was concluded that a) the morphology of UOCs is determined mainly by the chemical process (i.e. precipitation), and b) morphology is preserved by the calcination. However, even though it was observed that the particle shape was not affected by changing pH, temperature or reagent concentrations, it is assumed that the particle size and distribution can be affected by changing those parameters.

All list of references related to the application of isotopes and morphology to nuclear forensic origin assessment is compiled at the end of this chapter [2 - 5].

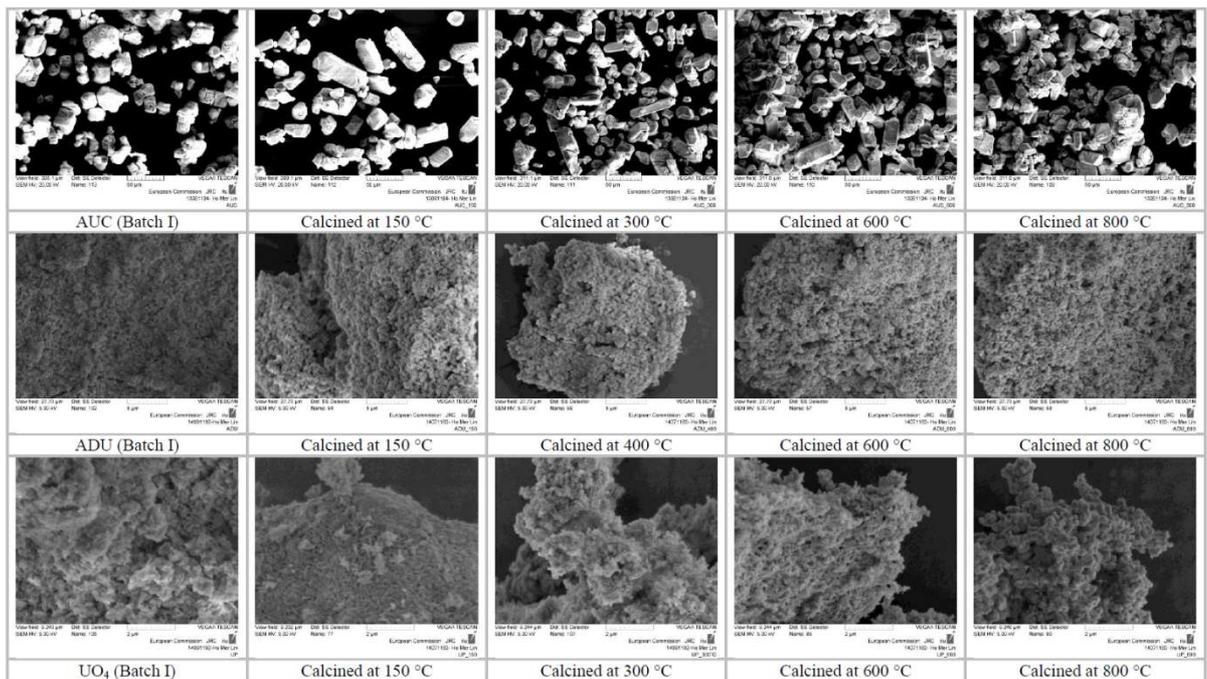


FIG. 6. Morphology of AUC, ADU and UO₄ after calcination in different temperatures.

3. CONCLUSIONS

Many promising signatures have been identified during the last few years in UOCs. However, as this study has demonstrated, only a few of them remain unaltered during the processing of ores to ore concentrates. In other words, those signatures that have been identified as being powerful for UOCs do not necessarily persist for more processed uranium samples (and vice versa). Elemental impurities are often measured as one of the first parameter in uranium samples, however this study has shown that every process stage changes the impurity pattern significantly. In consequence, only a few elements, e.g. REE and Pt-group elements, can be considered as useful for feed material (ore type) disclosure. Some other

elements can give information about the applied process, e.g. Mn if added as an oxidant. Furthermore, stable "radiogenic" isotope ratios found to be characteristic for certain ore deposit types, can be "diluted" during the process due to the contamination from the reagents by "natural" isotopic composition. This was found to be the case especially for Pb and to a lesser extent for Sr. Inhomogeneity of the ore bodies may also lead to perturbations in the signatures and will further complicate data interpretation. Therefore, "a critical view" during interpretation of the analytical results and the involvement of subject matter experts are recommended for data interpretation.

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PARAMETERIZATION OF UNKNOWN SPENT NUCLEAR FUEL FROM NUCLEAR REACTORS IN VIEW OF IDENTIFYING ITS ORIGIN

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1. INTRODUCTION

In this research investigation, an already established fingerprinting procedure is further assessed to discriminate conceptual and actual commercial spent nuclear fuels of different provenance based on the composition of the uranium and plutonium retrieved from the reprocessing of the spent fuel [1]. Furthermore, the research seeks to identify controls over this differentiation to include: the cooling time of the spent fuel, the plutonium 'age', the inclusion of ^{234}U and ^{236}U in the charge composition (conceptual fuels) and the location of a pin within a core (actual commercial fuel pins). Additionally, a multiple beam radiography procedure is assessed, through a simulation study, with the goal to qualitatively identify the possible presence of U and/or Pu in closed containers that might be intercepted as part of a nuclear security investigation.

2. WORK CONDUCTED

2.1 PROCEDURE

2.1.1 Isotopic fingerprinting for discriminating spent fuels

The procedure is based upon the composition of the U and Pu retrieved from the reprocessing of the spent fuel. Considering that the composition is inherently consistent and reflects the consequence of the fuel fresh composition, the neutron spectrum and the irradiation history, the composition carries information which can be uniquely related to the provenance of the fuel. The isotopic compositions, in the form of isotopic ratios, were in the case of (U, Pu) or Pu: $^{242}\text{Pu}/^{240}\text{Pu}$, $^{238}\text{Pu}/\text{Pu}$, $^{240}\text{Pu}/^{239}\text{Pu}$, $^{235}\text{U}/^{238}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$, $^{242}\text{Pu}/^{238}\text{U}$. Through the comparison of the isotopic ratios of the different spent fuels using multivariate statistical analysis (factor analysis), similar ratios are sought, allowing clustering of the spent nuclear fuels with the same origin [1- 5].

The procedure was assessed using simulated conceptual compositions of commercial and emerging spent nuclear fuels, as well as actual compositions of commercial fuels from a pressurized water reactor (PWR), boiling water reactor (BWR) and liquid metal fast breeder reactor (LMFBR). In the case of conceptual fuels, fresh fuel compositions based on U, with and without Gd as the burnable absorber, and Pu were assumed charged to the reactors. The U fuels were enriched in ^{235}U by 2.5-5% (PWR) and 2-4% (BWR), while the U/Gd fuels were enriched by 3.5%. Fresh fuels contained 300 and 600 mg kg⁻¹ ^{234}U and ^{236}U that represent concentrations which are at the upper end in actual commercial fuels. For each enrichment, the U and Pu isotopes have been simulated for spent fuels with a burn-up range of 30-50 GWd/tU (PWR & BWR) and 60-100 GWd/tU (LMFBR).

The emerging spent fuel cases included: fresh nuclear fuels containing either 1% ^{237}Np or ^{241}Am resembling their homogeneous transmutation in the commercial LMFBR-MOX, fuel with plutonium from its self-generated recycling in an LMFBR as well as fuels with plutonium or minor actinides from their self-generated recycling in a PWR. First generation plutonium has been considered from a PWR-U (3% ^{235}U), with an isotopic vector for 238/239/240/241/242 of 3.1/49.4/23.37/15.3/8.83, in the cases of conceptual commercial PWR- and LMFBR mixed oxide (MOX) and LMFBR-MOX transmutation fuels.

The Pu and minor actinide (MA) composition of the fresh fuels, in the self-generated recycling cases, are considered following 5 recycling steps (PWR) or 16 recycling steps (LMFBR). These recycling steps correspond to the period necessary to achieve an ‘equilibrium’ content of the recycled nuclides, with the same amounts formed and recycled.

The simulations of the conceptual commercial and transmutation fuels have been performed using the isotope generation and depletion code ORIGEN-ARP, within SCALE 6.1, and ORIGEN-2.2 [6, 7]. The nuclear data from the ENDF/B-VI [8] and ENDF/B-V libraries have been employed [9].

Furthermore, real spent fuel pins from PWR and BWR nuclear power stations have been considered. Composition and burn-up information of these fuels have been drawn from the SFCOMPO databank by OECD/NEA and are shown in Table 1.

TABLE 1. PWR AND BWR UO₂ FUELS CONSIDERED FROM THE SFCOMPO DATA SET.

REACTOR	REACTOR TYPE	FRESH FUEL (enrichment in ²³⁵ U)	BURN-UP RANGE (GWd/tU)
Obrigheim (pin 1)	PWR	3.00%	22 - 31
Obrigheim (pin 2)	PWR	3.00%	21 - 34
Obrigheim (pin 3)	PWR	3.00%	15 - 30
Monticello (pin 1)	BWR	1.87%	43 - 55
Monticello (pin 2)	BWR	1.87%	51 - 47
Gundremmingen (pin 1)	BWR	2.53%	21 - 26
Gundremmingen (pin 2)	BWR	2.53%	15 - 18

2.1.2 Multiple beam radiography

On first approach, neutron and photon beams have been used in a multiple beam radiography scheme. In this way, a range of energies of neutrons and photons are incorporated since their difference in absorption by different materials could enhance material discrimination. The required simulations were carried out using the MCNPX Monte Carlo Code [10]. An object can be characterised by means of the transmission of neutrons and γ rays through it. In the case of narrow-beam geometry, the transmission of fast neutrons and γ rays through the object are given by:

$$\frac{I_n}{I_n^0} = e^{-\mu_n \rho x} \Rightarrow R_n = \ln(I_n / I_n^0) \quad \text{and} \quad \frac{I_g}{I_g^0} = e^{-\mu_g \rho x} \Rightarrow R_g = \ln(I_g / I_g^0)$$

where, ρ and x are the density and thickness of the object, μ_n and μ_g are the neutron and γ ray mass-attenuation coefficients respectively, I_n and I_g are the transmission intensities through the object and I_n^0 , I_g^0 are the intensities of the neutron and γ ray beams. The ratio R , of the neutron and γ ray attenuation coefficients is:

$$R = \frac{R_n}{R_g} = \frac{\mu_n}{\mu_g} = \frac{\ln(I_n / I_n^0)}{\ln(I_g / I_g^0)}$$

Hence, the value of R , is independent of the thickness of the object; however, it depends on the composition of the material comprising the unknown object. An accurate determination is required in order to better characterise the object. The composition of the material interrogated by the beam would be inferred through comparing the measured R value with corresponding ones covering a range of possible

candidate materials. In the absence of sufficient experimental data, R values are created through simulations.

2.2 RESULTS

2.2.1 Isotopic fingerprinting for discriminating spent fuels

The clustering of the simulated conceptual PWR and BWR spent fuels, considered in this study, is shown in Figure 1. The potential of the procedure involves differentiation of spent fuels of: (1) different fresh composition of ^{235}U from the same reactor type; and, (2) the same fresh composition of ^{235}U from the PWR and BWR. On the basis of the U, Pu ratios considered, spent fuels are clustered in two distinct families according to the reactor type where the fuels were irradiated, namely PWR and BWR. Each one of the curves reflects a spent fuel of a particular enrichment originating from either PWR or BWR. Along each curve, each point corresponds to a burn-up of the particular spent fuel. Resolving the two reactor families improves with increasing burn-up. Within the PWR or BWR spent fuel families, the fuels are resolved from each other on the basis of their enrichment. The U/Gd based fuels discharged from the PWR and BWR are well discriminated as well as from the other spent fuels.

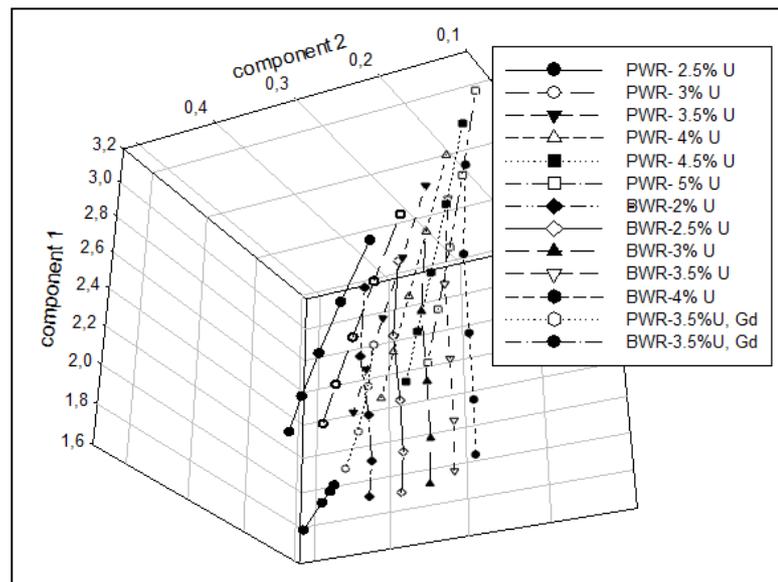


FIG. 1. Clustering of the PWR and BWR conceptual spent fuel cases considered, based on their (U, Pu) composition.

The procedure is extended to include the conceptual commercial and emerging spent fuels from PWR, BWR and LMFBR, and it is sensitive enough to discriminate the simulated spent fuels, yielding three distinct groups on the basis of their reactor type and charge composition (Fig. 2): the PWR- and BWR-U, the LMFBR cases and the PWR recycling schemes. The PWR- and BWR-U cases corresponding to fresh fuels of the same enrichment at 3.5%, are resolved on the basis of the different reactor type. The PWR-MOX and self-recycling schemes are resolved between them on the basis of their charge composition. Finally, the commercial LMFBR case is discriminated from the spent fuels of the transmutation and self-recycling schemes, due to the plutonium and other actinides composition in the fresh fuels.

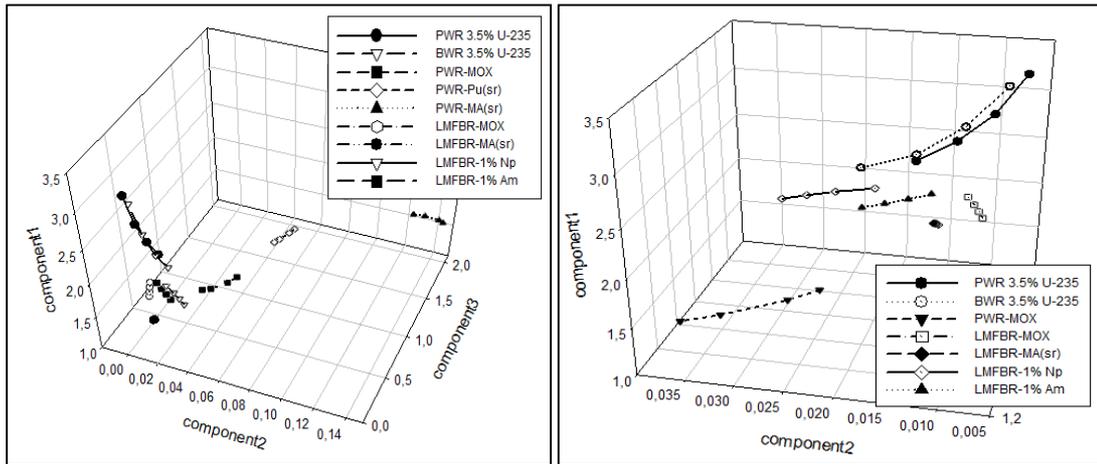


FIG. 2. Discrimination of conceptual simulated commercial and emerging spent fuels (left), with an improved resolution for the left half of the graph (right).

The information of the PWR- and BWR- UO_2 commercial spent fuel pins used is given in Table 1. The different spent fuel pins from the Obrigheim PWR, with the same enrichment of 3% (pins 1-3), are differentiated internal to the reactor core, indicating a dependence on the pin location within the core (Fig. 3). Similarly in the BWR cases, the pins are clustered together according to their reactor of origin; however, within each group the pins are discriminated internal to the reactor core indicating the dependence on the pin location within the core (Fig. 4). These results are obtained with the procedure based on (U, Pu) and Pu compositions.

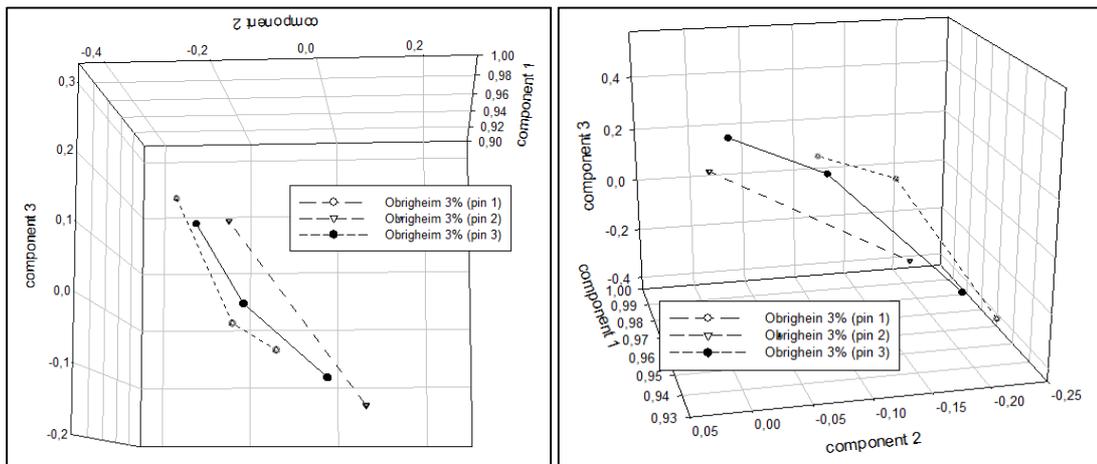


FIG. 3. Clustering of the PWR spent fuel cases considered, based on their (U, Pu) (left) and Pu (right) composition.

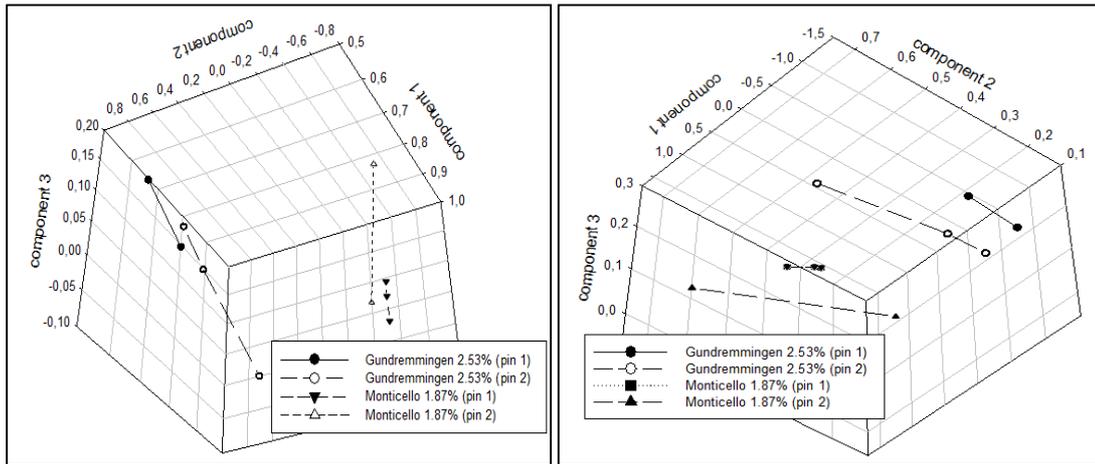


FIG. 4. Clustering of the BWR spent fuel cases based on their (U, Pu) (left) and Pu (right) composition.

The sensitivity of the procedure on the pin position within a core was further explored for the case of the PWR Obrigheim commercial reactor. Hence, pins of the same charge composition in ^{235}U and irradiation history, occupying different places within a 14x14 square assembly, have been considered. The schematic of the 14x14 square assembly is shown in Figure 5, as well as the positions of the four pins (inset). The local burn-up values at five sampling points along the active length of the pins are indicated. The burn-up values are different although the enrichment and irradiation history of the pins are the same.

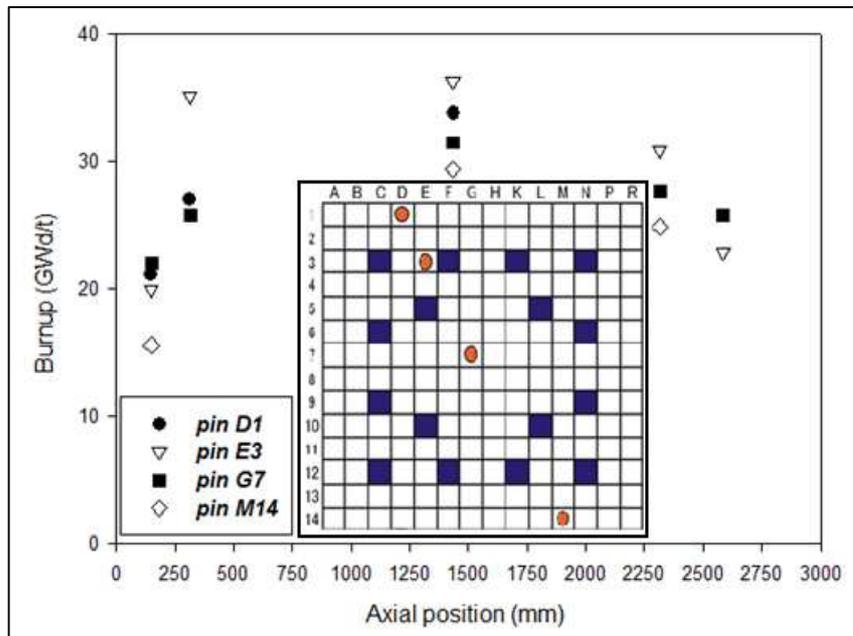


FIG. 5. Axial burn-up values along pins from the same assembly and positioning of the pins within the assembly.

The different burn-up values are attributed to the difference in neutron flux and spectrum at the different pin locations. Two pins occupy outside positions (D1, M14) while the others are in inner central positions within the assembly (E3, G7) with E3 next to a control rod. The assembly has been shuffled between the outside and the inside of the core, remaining there for 1 and 2 cycles of the reactor operation respectively. Furthermore, the assembly remained during one of the cycles between control rod assemblies. The pins have attained different burn-ups, and consequently (U, Pu) isotopics, indicating the dependence of their location within the core. Consequently, the required ratios of the Pu isotopes

determined through simulations should cover their three dimensional dependence within a core if supporting experimental data are unavailable.

This procedure is demonstrated for concentrations of the Pu isotopes at the end of irradiation (EOI) of fuels in the reactors. However, in nuclear forensics, the EOI and the time of the reprocessing of the discharged spent fuel for the retrieval of the Pu are unknown. After EOI and until reprocessing, the Pu isotopics will change due to the radioactive decay of ^{238}Pu ($\tau_{1/2}= 87.75\text{y}$) and ^{241}Pu ($\tau_{1/2}= 14.4\text{y}$) and the generation of ^{238}Pu , ^{239}Pu and ^{240}Pu from the radioactive decay of Cm isotopes with half-lives of 163d, 29.1y and 18.1y respectively. Following the Pu retrieval at the stage of reprocessing, the Pu isotopic composition would similarly change due to their radioactive decay.

The dependence of the procedure on the cooling time of the spent fuel from EOI up to its reprocessing and the ‘age’ of the Pu following its retrieval was examined for the conceptual case of PWR-U spent fuels with enrichments in the range of 2.75% to 4%. Further to the spent fuels with U, Pu ratios at EOI, their 50 GWd/tU ‘samples’ are plotted having different cooling times and Pu ‘age’ (Fig. 6). These ‘samples’ correspond to the conceptual fuel cases with enrichments 3.25%, 3.5% and 3.75%. The three ‘samples’ are considered with their Pu corresponding to an ‘age’ of 1, 5 and 10 years following retrieval 1.5 (*) and 5 (+) years after EOI (Fig. 6). In each of the three 50 GWd/tU cases, the ‘samples’ with the different Pu ‘ages’ are grouped together, indicating that the methodology is independent of the Pu ‘age’. This is due to the fact that the ^{241}Pu , with the shorter half-life (14.4 years) of the Pu isotopes, contributes only to the total Pu, while it is not used directly in a ratio. This is advantageous over previous studies, where ^{241}Pu was used directly complemented by multivariate statistical techniques, since a dependence of the methodology on a Pu ‘age’ beyond 0.5 years was observed [3]. A dependence of the methodology is observed on the cooling time of the ‘samples’, with the one corresponding to 5 years displaced from EOI (Fig. 6). Nevertheless, in all cases the ‘samples’ are grouped together with their corresponding spent fuels at EOI.

The methodology is further assessed, in case ^{234}U and ^{236}U are not included in the fresh composition of the simulated conceptual commercial PWR-U fuels. The spent fuel with 4% enrichment, simulated without ^{234}U and ^{236}U at charge, is now displaced (Fig. 6). The displacement increases with burn-up to 12% at 50 GWd/tU. The main contribution (99%) arises from ^{236}U due to the further generation of ^{238}Pu directly used within a ratio.

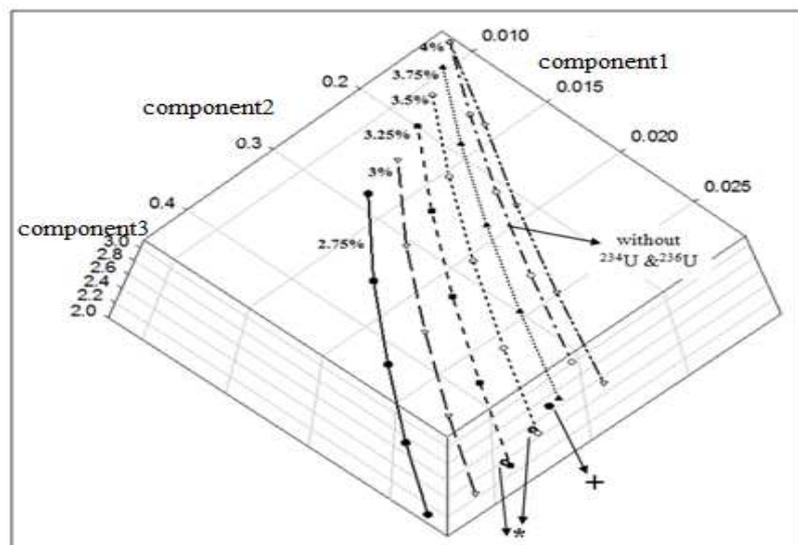


FIG. 6. Clustering of the PWR spent fuel cases considered.

2.2.2 Multiple beam radiography

A narrow beam geometry is employed in the simulations, with the collimated detector and source on either side of a cubical object. The calculated R values for different compositions inside the cubical object are shown in Figure 7. The compositions considered were 100%²³⁵U, 75%²³⁵U 25%²³⁹Pu, 50%²³⁵U 50%²³⁹Pu, 25%²³⁵U 75%²³⁹Pu, 100%²³⁹Pu. The R₁, R₂ R₃ values are shown as coordinates on the 3 dimensional graph, in the case of deuterium-deuterium neutron generator (NG) (E_n=14 MeV), a fission spectrum (FS) (²⁵²Cf neutron source, E_n=2 MeV) and the gamma ray sources

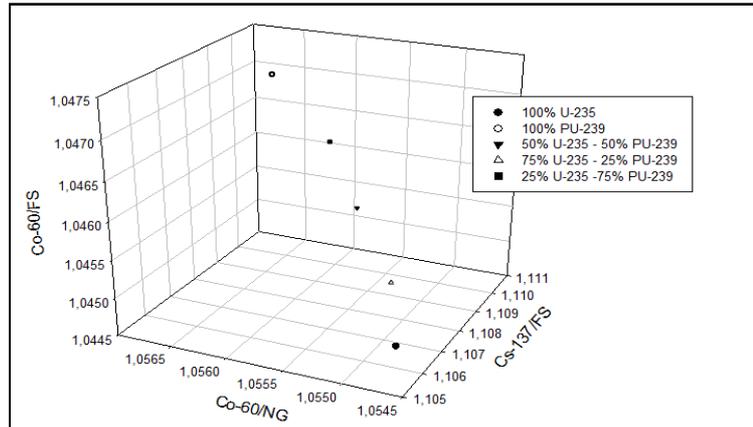


FIG. 7. Discrimination of different compositions of U, Pu inside a cuboidal object using a 4-beam neutron radiography.

¹³⁷Cs (E_γ=0.662 MeV) and ⁶⁰Co (E_γ= 1.172 and 1.332 MeV). These values were calculated with the MCNPX Monte Carlo code, using the *F1 tally card which gives the energy over a detector surface in MeV. Calculations were carried out for $\leq 10^{10}$ histories for neutrons and gamma rays, achieving a favourably accuracy (errors less than 0.05% in all cases). Although of close mass number, the materials are clearly discriminated.

3. CONCLUSIONS

Fingerprinting, based on ratios formed from the use of U and/or Pu isotopic composition, is studied to discriminate spent fuels of different provenance. Conceptual simulated and real spent fuels have been used, originating from PWR, BWR and LMFBR charged with different enrichments of U, UGd and Pu fuels. The methodology was sensitive enough to resolve enrichments from different reactor types. The discrimination of actual spent fuel pins representing spent fuels of different enrichments from the same reactor type as well as from the same enrichment from an assembly indicates that the procedure depends on the pin location within the core. The fingerprinting procedure is independent of the Pu ‘age’, however dependence is observed relative to the cooling time of the spent fuels. In the case of the simulated fuels, the procedure is significantly influenced by the inclusion of ²³⁶U in the charge composition of the fuel. In a simulation study, the use of multiple neutron and gamma beams, resembling radiography, has successfully discriminated different combinations of amounts of ²³⁵U and ²³⁹Pu, ranging between 0% and 100%, within a cuboidal object.

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ESTABLISHMENT OF A NATIONAL LIBRARY FOR NUCLEAR FORENSICS PURPOSES IN HUNGARY

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1. INTRODUCTION

In the frame of the IAEA Coordinated Research Project J02003 the Hungarian Academy of Sciences Centre for Energy Research (MTA EK) planned the following tasks within the three year research window:

- a comprehensive review of relevant publications to include a search for promising new methods to find the high confidence nuclear forensics signatures;
- analysis of nuclear materials seized by the Hungarian authorities to obtain relevant signatures useful for the development of a national nuclear forensics library. The following techniques, available at the Centre for Energy Research were used for this purpose including: physical characterization, optical and scanning electron microscopy, gamma-spectrometry, mass spectrometry, X ray diffraction and X ray fluorescence techniques as well as prompt gamma activation analysis;
- statistical analysis and evaluation of the relatively large and informative database obtained by the analysis to find relevant signatures;
- establishment of a national nuclear forensics library programme in Hungary;
- overview of potential forensic signatures of radioactive sources.

2. WORK CONDUCTED

2.1 ANALYSIS OF NUCLEAR SAMPLES IN HUNGARY

As part of this research, MTA EK analysed approximately 80 nuclear material samples derived from past seizures in Hungary, materials used in Hungarian nuclear reactors, as well as samples used in inter-laboratory comparison exercises [1]. The samples comprised uranium-oxide pellets, uranium-oxide powders, metallic uranium, uranium ore concentrates (yellow cake) and normal laboratory reagents (e.g. uranium-nitrate, uranium-acetate, thorium-oxide, etc.). Repeated analyses were performed using the same unit of a sample (e.g. the same pellet) and using items from the same batch (e.g. more pellets from the same confiscation).

Various techniques and methods were used for the analysis and characterization of the samples to include: full physical characterization, morphology study, uranium isotopic composition (using gamma- and mass-spectrometry), impurities to include rare earth element (REE) and other elemental content, lead isotope ratios, age dating (using gamma- and mass-spectrometry), plutonium isotopes, reprocessing, chemical composition as well as analysis of organic impurities.

The commonly used analytical techniques consisted of mass spectrometry, gamma spectrometry, X ray diffraction (XRD), X ray fluorescence (XRF), Fourier-transformation infrared spectroscopy (FTIR), scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS) and optical microscopy.

Some new/novel techniques and methods were also introduced for molecular studies. These techniques were: laser induced break-down spectroscopy (LIBS), XRF-RAMAN coupled system and electron spectroscopic techniques to include x ray photoelectron spectroscopy (XPS) and electron spectroscopy for chemical analysis (ESCA).

Intermediary layer/surface contamination of pellets using the XPS/ESCA technique as well as the determination of the oxidation-forms of pellet samples were novel parameters studied as part of the research.

A significant finding from the research was that a single signature cannot answer all the questions concerning the origin and history of nuclear and other radioactive material in a majority of cases. Using a combination of different signatures can be most useful to determine provenance depending on the type of the material.

2.2 STATISTICAL EVALUATION OF THE ANALYTICAL RESULTS

All the data obtained from the analysis were statistically evaluated relative to their utility to identify the origin of an unknown material using different types and combinations of data characteristics (i.e., signatures).

In the case of uranium fuel pellets or uranium-oxide powders, physical and morphological characteristics (signatures) are relevant since they can indicate the production technology. Age (production date) is also a key high confidence signature, as well as the traces of ^{236}U or plutonium isotopes that are indicative of reprocessed material.

Results of age dating studies were notable. Within a single seizure and same batch of samples (i.e., a large number of pellets in a package) that all displayed the same physical characteristics, different production dates were found among samples. This result draws attention to the need for careful and systematic sub-sampling of a larger inventory of samples with seemingly the same characteristics.

Elemental impurities are not relevant in the case of uranium-oxide samples due to the high purification of uranium (e.g. high dilution of REE content), the contamination of the material during the various technological processes of production as well as the inhomogeneity of the material even within a single pellet (elemental fractionation during the crystallization). Only select elements are introduced to the raw material for any technological purposes and therefore, can serve as relevant indicators of production processes (e.g. Mg, V, Gd, Eu and W). Following our experience, any other elemental profiles in the case of uranium-oxide samples were found to be useless including the commonly used lead isotopic ratio (due to the inherently high contamination originating from the production technology and the dilution of lead during the technological steps).

In the case of laboratory reagents we also found some key elements which serve as high confidence signatures because they reflect the production technologies and therefore the producer. These signatures are: ^{236}U , V, Mg content and Pb isotopes. Age can be also determined in the case of the reagents.

2.3 NATIONAL NUCLEAR FORENSICS LIBRARY (NNFL) PROGRAM

The first prototype of the NNFL programme in Hungary was established and tested. The programme contains data collection and storage functions as well as searching/comparative, identification and reporting features that utilize nuclear forensic relationships between samples and signatures.

The programme is based on a relational-database-handling system. It uses the commonly applied SQL (structured query language) data-definition language and combines the object-relation and deductive relation. Presently Linux® and Windows® based servers operate the library platform in secure mode (https and url).

The system runs with unique, custom (i.e., in-house) developed program codes (using C++, Visual Basic and php webcode), which facilitates access through an internet browser without compatibility problems.

There are 4 authorization levels with entry permission: i) system admin with full authorization, ii) the user (point of contact), iii) the laboratory staff with permission for data uploading only and iv) the nuclear forensic expert (SME) for data evaluation.

The library platform supports the Hungarian and English languages.

The national nuclear forensics library software is adaptable and expandable to reflect contingencies associated with development and sustainability of the national nuclear forensic library. The primary advantage of the program is that it is intelligent: the program is easy to update and to add any new information (parameter/signature/others) into the system any time.

In the searching or data-comparison function it is possible to choose special, relevant or individual signatures to identify agreement among samples, as well as to use all additional and available parameters.

2.3.1 File formats

The library software architecture allows for the addition of *.pdf reports, pictures and spreadsheet sheets into the program, as well as to upload digits into tables and categories with a copy-paste function. For the searching function digits and simple words can be used. All the data can be uploaded into data-package boxes. User interface colors indicate that data are already uploaded (green color) or still missing (empty/white boxes) (Fig. 1).

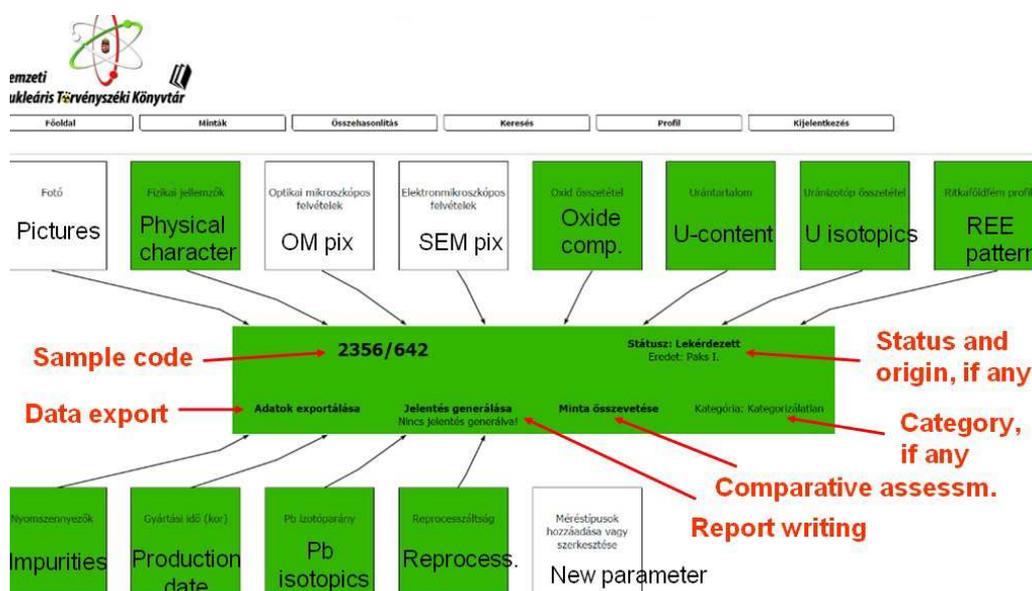


FIG.1. Data system connected to a sample.

When uploading sample information into the system it will be put into the “zero” category. Since the “state” of the analytical data is tracked continuously, if there is already enough information about the sample it will be possible to move it into its own category. Later, if the origin of the sample is determined, it is possible to add this information to the sample descriptors (indication of origin). Samples in the library software are indicated with colors depending on their sub-categories like: “national use”, “confiscated”, “requested” and “others”.

2.3.2 Reporting function

The database is designed to compile all the data on a sample in one report. Another possibility is to obtain sub-reports in different stations of the identification procedure. After the identification and comparison procedure all the data on samples in agreement is exported into an excel file. Similar data from samples are presented in the same line in the spreadsheet, therefore, it is easier for the subject matter expert (SME) to compare the results as an aid in interpretation.

Twelve categories are determined in the system reflecting the stages of the nuclear fuel cycle and consistent with draft guidelines from the IAEA and Nuclear Forensics International Technical Working Group (ITWG). Further sub-categories within each category of the 12 are planned (e.g. within enrichment: UF₆, UF₄, or within fresh nuclear fuel: U₃O₈, UO₂, powder, pellet, etc.); other categories have already been added like those for sealed radioactive sources.

2.3.3 Functioning of the library

If there is a request or question from another country related to the origin of confiscated material (i.e. “Is it our material?”), there are two possibilities to handle the data involving the questioned sample. In the first case, it is possible to store the data as sample information if the other county approves this storage. In this instance, the sample will be indicated with a marking: “required sample”. However, if the data are sensitive and storage is prohibited, there is a possibility to add only the sample data externally and after obtaining results from comparison; this sensitive data will not be stored (it will be automatically deleted - see Fig. 2).

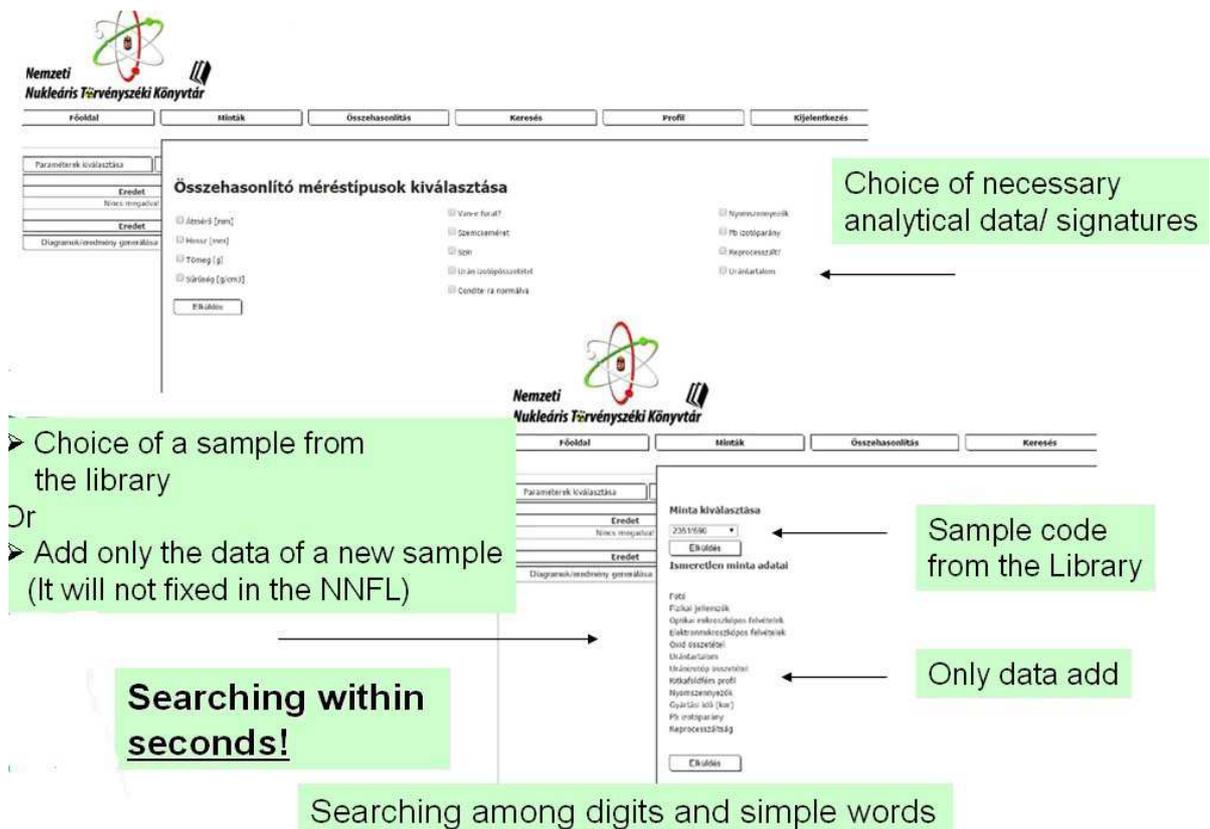


FIG. 2 Searching or data-comparison function in the library system.

The database comparison function works within seconds even if all signatures are employed. It is possible to upload all available signatures, but for searching (data-comparison) it is also possible to choose only some signatures which seem relevant depending on the case. The program is designed to be flexible and use only relevant signatures for searching.

Findings (agreement among samples) based on numerical data (e.g. age, isotopic enrichment, etc.) and simple words (e.g. for example, a light grey color) are indicated with ticks. Samples found with data similar to the requested sample can be chosen and all the data for further investigation by a subject matter expert (SME) can be exported into a spreadsheet file.

A special function of the library database is that the rare earth element (REE) pattern as a nuclear forensic signature can be visualised immediately among requested and identified samples within one figure (Fig. 3).

It is important to emphasize that while the library program is an intelligent tool for statistical evaluation of the results of a nuclear forensics examination and as an aid for the subject matter expert, the program alone cannot substitute for the human factor or the role of a SME who utilizes his/her expertise in nuclear analysis and knowledge of the nuclear fuel cycle to inform the answers to a nuclear security investigation. The role of subject matter experts remains a key factor in the confidence of nuclear forensic findings.

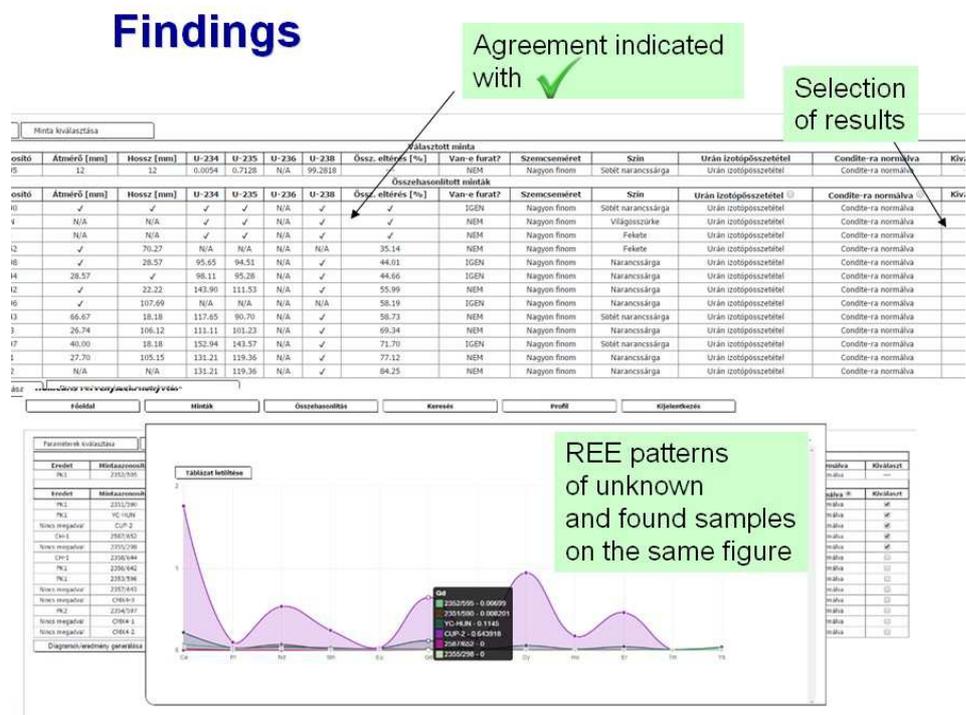


FIG. 3. Agreement among samples – origin assessment.

Nuclear forensic analytical results from 80 samples are presently uploaded into the library system and it was also tested using virtually generated data of “hypothetically seized” samples. Further improvements to the program are planned and are in progress already.

2.3 OVERVIEW OF POTENTIAL FORENSIC SIGNATURES OF SEALED RADIOACTIVE SOURCES

There are several commonly used sealed radioactive sources which contain impurities that may be exploited as part of a nuclear forensics examination. Impurity isotopes can identify the sealed radioactive source. Table 1 contains some typical impurities and their origins in sealed sources.

TABLE 1. IMPURITIES IN SEALED RADIOACTIVE SOURCES

Principal nuclide (i.e., type of the source)	Impurity nuclide	Remarks
Ir-192	Co-60	The half-life of Ir-192 is 73.8 days. The half-life of Co-60 is 5.27 years; therefore as Ir-192 decays, Co-60 will be present in the source.
Cs-137	Cs-134	Same element. Both of these isotopes are fission products. The half-life of Cs-134 (2.07 years) is much shorter than Cs-137 (30.07 years), therefore using this isotope the age of the source can be estimated.
Eu-152	Eu-154	Same element, half-life is similar.
Co-60	Cs-137	The reason is not determined. Contamination at the producer's facility (laboratory or applied tools during the production) is possible.

Cobalt-60 radioactive sources produced in 1960 were measured by low-background gamma-spectrometry at our laboratories. Measurement data show that a ^{137}Cs impurity was found in addition to the ^{60}Co main isotope in the source. The presence of ^{137}Cs indicates contamination occurred during the packaging/encapsulating of the material because the presence of ^{137}Cs during the production of ^{60}Co is not possible by nucleonic interactions. The presence of ^{137}Cs can be an indicator of production technologies especially for special producers/conditions.

Cobalt is frequently a contaminant in iridium radioactive sources because iridium metal contains natural cobalt due to their similar chemical properties and can be a signature of the origin of the source material.

2.4 PRACTICE FOR NATIONAL NUCLEAR FORENSICS LIBRARY SYSTEMS

MTA EK participated in the ITWG web-based virtual table top exercises Galaxy Serpent version 1 and version 2 conducted in 2013 and 2015, respectively. The exercises focused on how to establish and use a national nuclear forensics library to find the origin of nuclear or other radiological materials in a hypothetical scenario. Following our experiences in these exercises and from our practical work, the data characteristics (signatures) of sealed radioactive sources that can be useful for origin assessment include: current activity and reference activities/dates; physical characterization (size, description, capsule material, structural material, impurities, etc.) including photos and drawings as well as type of source.

Other key parameters of sealed radioactive sources include: model and serial numbers and other accompanying documentation, as well as markings on the shielding container and capsule. To note, these parameters are often missing in most cases.

3. CONCLUSIONS

The majority of the scientific and technical goals of Hungary were achieved as part of the involvement in IAEA CRP J02003; however some original plans were changed during the course of the investigation following our results and experiences.

The first prototype of the NNFL is available in Hungary. It is currently undergoing further testing and additional improvements will be incorporated. These include:

- An electronic system incorporating analytical and laboratory quality assurance and custodial signatures supporting an evidentiary chain-of-custody;
- Direct contact and access to the library from the laboratories and radiological crime scene in real time (mobile laboratory, using e.g. tablets and wireless internet protocols); and,
- One-channel secured communication.

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MASS SPECTROMETRY, RADIOMETRY AND OTHER ANALYTICAL TECHNIQUES FOR NUCLEAR FORENSICS

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1. INTRODUCTION

Development of a national nuclear forensics library is of interest to States from the point of view of meeting their nuclear security obligations [1]. Success in this endeavour depends upon two important factors: (i) availability of materials from different facilities involved in different stages of the nuclear fuel cycle (NFC) and (ii) analytical instrumentation and expertise available within the Member State for robust analysis and data interpretation. Since India has adopted a closed nuclear fuel cycle and has the capabilities for producing materials indigenously at different stages of the nuclear fuel cycle (NFC) starting from mining, milling, fuel fabrication and reprocessing, the development of a national nuclear forensics library is of great significance to India and will be a national asset.

2. WORK CONDUCTED

2.1 A NUCLEAR FORENSIC CAPABILITY

In our research centre, instrumentation and expertise is available for performing a variety of measurements to meet the objectives of nuclear forensics for various materials encountered at different stages of the NFC. These measurements include isotopic composition determination, trace impurities analysis, phase analysis, morphology, speciation and microanalysis. As an example, a large amount of data has been generated on isotopic composition of plutonium by thermal ionization mass spectrometry (TIMS) in irradiated fuels from different research and power reactors. These data have been produced as a part of chemical quality assurance of nuclear fuels as well as for nuclear materials accounting and have been used to develop useful isotope correlation among different isotopes of Pu. Isotope correlations have been established among $^{238}\text{Pu}/(^{239}\text{Pu}+^{240}\text{Pu})$ alpha activity ratio determined alpha spectrometrically and $^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$, $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratios obtained by TIMS. By employing chemometrics analysis using principal component analysis (PCA), it has been shown that Pu generated from research reactors with an average burn-up of 1000-1500 MWD/TU can be easily discriminated from Pu formed in pressurized heavy water reactors (PHWRs) with an average burn-up of about 10,000 MWD/TU. In addition, using Pu isotopic composition data available in the open literature for pressurized water reactors (PWRs) and other types of reactors, it has been shown that such isotope correlations can easily discriminate Pu available from different types of reactors. Hence, these correlations are very useful for nuclear forensics.

2.2 RESULTS OF ANALYSIS

During the development of isotopic correlations, it was observed that the uncertainty obtained in ^{241}Pu abundance was large due to lack of information available to analysts on the irradiation and cooling history of irradiated fuels coupled with the short half-life of 14.4 years of this Pu isotope. Also, the uncertainty of the ^{242}Pu determination was large due to the fact that most of the isotope correlations developed to determine this isotope are empirical in nature and the ^{242}Pu content is quite small due to the low burn-up of irradiated fuels available indigenously. These limitations were overcome by developing a liquid scintillation counting (LSC) methodology for ^{241}Pu determination as well as by employing a multivariate regression approach for evaluation of ^{242}Pu isotope correlations. Different chemometric methods like multiple linear regression (MLR), principal component regression (PCR) and partial least squares regression (PLSR) were used to evaluate the different isotope correlations for ^{242}Pu

determination. A critical analysis of the isotopic composition data and of different correlations showed that the correlation involving data on ^{238}Pu content provides the highest accuracy for ^{242}Pu determination.

Another important measurement in nuclear forensics is the determination of the age of any interdicted Pu sample. The age refers to the time elapsed since last purification of Pu was done in the facility. The age of any Pu sample can be determined by employing ^{239}Pu - ^{235}U , ^{240}Pu - ^{236}U and ^{241}Pu - ^{241}Am radio-chronometers. It is always preferred to determine the age by utilizing more than one radio-chronometer to enhance the confidence in the age determination. The chronometer ^{238}Pu - ^{234}U is not employed due to the problem of ubiquitous isobaric interference of ^{238}U at ^{238}Pu during the determination of ^{238}Pu by TIMS. To overcome this limitation, a novel mass spectrometric methodology was developed and validated in our laboratory by carrying out studies on the formation of M^+ and MO^+ ions during the analyses of both U and Pu by TIMS. The methodology is based on the fact that UO^+ and PuO^+ ions are produced at different heating temperatures of the ionization and vaporization filaments. By adding a small amount of enriched ^{235}U (>90% ^{235}U enriched) to the unknown Pu sample followed by determination of the $^{235}\text{U}/^{238}\text{U}$ ratio using UO^+ , the isobaric interference of ^{238}U at m/z 238 can be accounted for by employing ^{235}U as a monitor isotope and applying an interfering element correction methodology available in the TIMS software. This methodology was validated by preparing and characterizing synthetic mixtures prepared by mixing, on a weight basis, the solutions of enriched isotopes of ^{238}Pu and ^{239}Pu . This TIMS methodology will be highly useful for Pu samples generated from irradiated fuels with extended burn-up (30,000 to 40,000 MWD/TU) since conventionally used alpha spectrometry will have limitations due to tail contribution problems at higher percentages (>1 atom % or more) of ^{238}Pu .

3. CONCLUSIONS

Future work will entail validation of analytical techniques using certified reference materials of U and Pu and then applying these same techniques to indigenous materials available from different facilities within India. Further, with the availability of new facilities like a magnetic sector based secondary ion mass spectrometer (SIMS) and a high resolution laser induced breakdown spectrometer (LIBS), it is proposed to determine $^{18}\text{O}/^{16}\text{O}$ isotope ratios in different U samples and also perform the impurity analysis for comparing qualitatively the various impurities present in different U samples.

For determining the ages of different U and Pu samples, difficulties in obtaining enriched isotopes to be used as spikes in mass spectrometry hampers some international laboratories. The IAEA might potentially facilitate the availability of small amounts of the spike isotopes which can be used to validate the age determination methodology by using more than one radio-chronometer thereby enhancing the confidence in the data on age of U and Pu samples.

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IDENTIFICATION OF HIGH CONFIDENCE NUCLEAR FORENSICS SIGNATURES FOR MINING, MILLING AND CONVERSION PROCESSES

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1. INTRODUCTION

To address international concerns regarding the threat posed by nuclear and other radioactive materials out of regulatory control, it is crucial for Indonesia to have a national nuclear forensics library [1]. As a precursor to the development of such a library, identification of nuclear materials produced, used, stored, and transported in the country must be done as soon as possible. BATAN has research and development facilities to study nuclear material from the front end to the back end of the cycle of nuclear materials, incorporating mining, milling, refining processes, conversion, fuel fabrication, research reactors, spent fuel storage and handling of radioactive waste.

The first year of the coordinated research project (CRP) focused on the identification and characterization of UO_2 powder, UO_2 pellets and UO_2 fuel pins. The second year of the research focused on identification and characterization of uranium ore and yellow cake. The third year focused on the identification and characterization of uranium ore, yellow cake and UO_2 powder. Thus, the overall scope of research incorporated material studies of uranium ore, yellow cake, UO_2 and UO_2 fuel pins.

The identification of high confidence nuclear forensics signatures for all nuclear materials included in the scope of the project has been conducted using testing instruments available in the BATAN. The objective of the research work is to provide identification through characterization of all nuclear materials existing in national facilities.

2. WORK CONDUCTED

2.1 METHOD

The investigative method involves identification and characterization of nuclear material from mining, milling, conversion and nuclear fuel fabrication processes. Samples of all nuclear materials are identified and characterized relative their respective properties. Based on the IAEA implementation guide on nuclear forensics, there are approximately eight kinds of characterization data that needs to be taken to fully characterize nuclear material:

- For uranium ore, the characterization objective covers the geology, mineralogy, uranium concentration, uranium isotopes, stable isotopes and trace elements of the ores;
- For yellow cake, the characterization objective encompasses the chemical form, physical characteristics, morphology/crystallography, uranium concentration, uranium isotopes, uranium decay series radionuclides, stable isotopes, trace element concentrations and process information;
- For UO_2 , the characterization objective targets measurements of the physical characteristics, morphology/crystallography, chemical form, uranium concentration, trace elements, uranium isotopes, process information as well as properties of the container;

- In the case of a UO_2 fuel pin, the characterization objective involves determination of the physical characteristics, serial number, morphology/crystallography, chemical form, elemental concentration, trace elements, uranium isotopes as well as process information; and,
- The characterization is done by using available testing equipment to determine the properties of the nuclear materials:
 - Analysis of trace element concentrations using an atomic absorption spectrometer or neutron activation analysis
 - Determination of elemental concentration of uranium using potentiometric titration
 - Determination of surface roughness using surface roughness tester
 - Testing morphology using optical microscope
 - Mineralogy characterization using x ray diffraction (XRD)
 - Analysis of uranium isotopes using gamma spectrometry
 - Determination of chemical form (molecular form) using XRD
 - Density measurement using ultra pycnometer or XRD
 - Determination of morphology/crystallography using XRD, optical microscope and vibrating sieve

2.2 RESULTS

2.2.1 Uranium Ore and Ore Deposits (4 Samples of Uranium Ores From Different Mine Locations)

TABLE 1. GEOLOGY CHARACTERISTICS

Mine location	Eko Remaja	Sungai Marta	Tor Siandulimat, Sumatra Utara	Boteng, Mamuju
Geology formation	Malihan Pinoh Rock	Riolit Nyaa	Sibolga formation	Adang volcano formation
Deposit type	Vein type	Vulcanogenic	Sedimenter	Volcanic
Mining technique	Underground shrinkage stoping mine	-	-	-
Color	Grayish black	Blackish gray	Fawn	Fawn – Whitish

TABLE 2. MINERALOGY CHARACTERISTICS

Mine location	Eko Remaja	Sungai Marta	Tor Siandulimat, Sumatra Utara	Boteng, Mamuju
Mineral present	Uraninite, brannerite, davidite, and gummite	Pitchblende	Pitchblende	Thorianite
Chemical composition of mineral	Uraninite: UO_2 Brannerite: $(U^{4+}, Ca)(Ti, Fe^{3+})_2O_6$ (Uranium Calcium Titanium Iron Oxide) Davidite: $La_{0.7}Ce_{0.2}Ca_{0.1}Y_{0.075}U_{0.25}Ti_{1.5}Fe^{3+}_3O_8$ Gummite: $UO_3 \cdot nH_2O$	UO_2	UO_2	ThO_2

TABLE 3. URANIUM CONCENTRATION

Mine location	Eko Remaja	Sungai Marta	Tor Siandulimat, Sumatra Utara	Boteng, Mamuju
Uranium concentration in $\mu g/g$ (ppm)	1017	120	347	3000

TABLE 4. URANIUM ISOTOPES

Mine location	Eko Remaja	Sungai Marta	Tor Siandulimat, Sumatra Utara	Boteng, Mamuju
Isotope ratio $^{235}\text{U}/^{238}\text{U}$	0.0072975	0.0071953	0.0073904	0.0072616

TABLE 5. TRACE ELEMENT CONCENTRATION

Mine location	Eko Remaja	Sungai Marta	Tor Siandulimat, Sumatra Utara	Boteng, Mamuju
Trace element concentration in $\mu\text{g/g}$ (ppm)	Ce: 2318.51±11.49 Eu: 9.79±0.61 Hf: 38.16±4.85 La: 1138.65±3.62 Sc: 7.60±0.68 Sm: 222.93±2.14 Th: 30.42±6.51 U: 158.52±3.24	As: 1068.66±7.69 Ba: 7105.24±215.91 Ce: 4894.06±109.05 Co: 105.94±7.04 La: 872.13±1.80 Sb: 45.79±2.22 Sc: 15.22±0.30 U: 1.90±0.05	As: 804.21±3.62 Ce: 140.10±27.04 Cs: 46.09±2.77 Eu: 3.57±0.35 Hf: 17.09±1.85 La: 123.93±1.20 Sb: 21.13±1.11 Sc: 8.47±0.50 Th: 92.70 ±3.22 U: 1482.65±5.17	As: 1015.56±3.9 9 Ce: 632.82±17.63 Cs: 66.74±1.69 Eu: 3.59±0.36 Hf: 22.17±1.53 La: 162.74±1.17 Sb: 11.18±0.68 Sc: 9.44±0.27 Th: 109.18 ±1.86 U: 1843.39±4.37

2.2.2 Yellow Cake (3 Kinds of Yellow Cake from Cogema, Kalimantan and a Side Product of Phosphate Fertilizer Plant)

TABLE 6. CHEMICAL FORM

Chemical form	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
Compound name	Dioxouranium (VI) Hydroxide	Dioxouranium (VI) Hydroxide	Triuranium octoxide
Empirical formula	$(\text{UO}_2)(\text{OH})_2$	$(\text{UO}_2)(\text{OH})_2$	U_3O_8
Chemical formula	UO_4H_2	UO_4H_2	U_3O_8

TABLE 7. PHYSICAL CHARACTERISTICS

Physical Characteristic	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
Density	6.611 g/cc	7.031	8.479 g/cc

TABLE 8. MORPHOLOGY

Morphology	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
Lattice structure	Orthorhombic	Orthorhombic	Hexagonal
Color	Yellowish grey	Yellow	Blackish grey
Shape	Rounded	Sub rounded	Rounded

TABLE 9. URANIUM CONCENTRATION

Uranium Concentration	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
Uranium concentration in weight percent	76.23%	56.3%	50 – 60%

TABLE 10. URANIUM ISOTOPES (USING GAMMA SPECTROMETRY)

Isotope ratio	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
$^{235}\text{U}/^{238}\text{U}$	0.00715	0.00555	0.0064
$^{234}\text{U}/^{238}\text{U}$	-	0.00013258	0.000055823

TABLE 11. TRACE ELEMENTS (USING ATOMIC ABSORPTION SPECTROPHOTOMETRY)

Trace element	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
Trace elements	Ag, Al, B, C, Ca, Cd, Cl, Co, Cr, Cu, Dy, F, Fe, Gd, Mg, Mn, Mo, H, Ni, Pb, Si, Sn, V and Zn	Ag, Al, B, C, Ca, Cd, Cl, Co, Cr, Cu, Dy, F, Fe, Gd, Mg, Mn, Mo, H, Ni, Pb, Si, Sn, V and Zn	Ag, Al, B, C, Ca, Cd, Cl, Co, Cr, Cu, Dy, F, Fe, Gd, Mg, Mn, Mo, H, Ni, Pb, Si, Sn, V and Zn
Trace element concentration in $\mu\text{g/g}$ (ppm)	Ag: 0.14, Al: 2.75, B: 0.3, C: 100, Ca: 58.73, Cd: 0.05, Cl: 15, Co: 0.80, Cr: 3.15, Cu: 1.36, Dy: 0.15, F: 10, Fe: 48.68, Gd: 0.5, Mg: 25.57, Mn: 3.63, Mo: 10.92, H: 80, Ni: 2.58, Pb: 0.75, Si: 24.95, Sn: 10.03, V: 101.95 and Zn: 3.62	Ag:0.0677, Al:2860.49, B:-, C:-, Ca:5067.8684, Cd:0.0226, Cl:-, Co:2.2971, Cr:170.2889, Cu:8.2103, Dy:-, F:-, Fe:5.9740, Gd:-, Mg:435.8205, Mn:45.8631, Mo:<0.03, H:-, Ni:54.2139, Pb:13.938, Si:236.2416, Sn:0.4518, V:-, and Zn:1.4264	Ag: 0.047, Al: 3.97, B: 0.3, C: 100, Ca: 75.34, Cd: 0.07, Cl: 15, Co: 0.81, Cr: 3.81, Cu: 1.19, Dy: 0.15, F: 10, Fe: 18.53, Gd: 0.5, Mg: 25.12, Mn: 3.82, Mo: 23.67, H: 80, Ni: 1.86, Pb: 0.72, Si: 31.90, Sn: 6.32, V: 97.30 and Zn: 18.91

TABLE 12. PROCESS INFORMATION

Process information	YC COGEMA	YC Kalimantan	YC side product of phosphate fertilizer
Mining and milling process	Underground mine	Underground mine	Side product of fertilizer
Location of processing site	Cogema, France	Kalimantan, Indonesia	Petro Kimia Gresik, Indonesia

3. CONCLUSIONS

The coordinated research has allowed identification of a variety of nuclear materials encountered in Indonesia. These results were compiled with a limited inventory of analytical equipment; for example, Indonesia does not presently maintain a mass spectrometry laboratory. To measure the isotope ratios of uranium, gamma spectrometry is routinely employed. Indonesia has a scanning electron microscope facility but this instrument is inoperative. Using existing capabilities coupled with knowledge of subject matter experts, Indonesia continues to perform identification and characterization for all nuclear materials under national custody. Indonesia is presently establishing a data base containing data characteristics of all of these nuclear materials to facilitate nuclear forensic interpretation.

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SIGNATURES FOR NUCLEAR FORENSIC INVESTIGATIONS

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1. INTRODUCTION

During the current Coordinated Research Project, nuclear forensic studies at the Swedish Defence Research Agency mainly focused on two topics: characterization of strong ^{241}Am -sources and measurements of lanthanides in uranium matrices.

2. WORK CONDUCTED

2.1 CHARACTERIZATION OF STRONG ^{241}Am SOURCES

The research on characterization of strong ^{241}Am sources concentrated on investigating gamma spectrometry as a tool for finding inherent signatures that would make it possible to discriminate between different ^{241}Am sources in cases where immediate visual signatures were not present. The current study was aimed to investigate whether gamma ray spectra of strong ^{241}Am sources could disclose hidden information about source composition as other radioactive nuclides such as progeny and radioactive impurities might be revealed by extensive gamma ray spectra analysis.

A number of high activity ^{241}Am sources were measured using gamma spectrometry and the resulting spectra were compared to detect relevant signatures. The investigation focused on signatures such as age, i.e. time passed since last chemical separation and impurities. The results showed that ^{241}Am and its progeny ^{233}Pa could be used for age determination. Of further significance, it was found that nuclear reactions occurred in sources with low Z impurities such as sodium and magnesium. Alpha particles react with a low Z nucleus, which in turn may emit a neutron or a proton. The resulting nucleus de-excites or decays resulting in emission of characteristic gamma rays. This shows up as Doppler-broadened peaks in the gamma spectra. Furthermore, the investigation identified ^{243}Am as a possible impurity in some sources. In two of the five spectra for the investigated ^{241}Am sources, peaks of ^{239}Np were identified. This indicates that these sources contain ^{243}Am as an impurity, since ^{239}Np is the daughter of ^{243}Am .

The spectral features identified in this work would be useful information in a national nuclear forensics library (NNFL) in cases when visual information concerning the source, e.g. a source serial number, for various reasons might be limited or not available. The full results of this research have been reported elsewhere [1].

2.2 INVESTIGATION OF INTERFERENCE-FREE LANTHANIDE MEASUREMENTS USING MASS SPECTROMETRY

The lanthanide series has been identified as a suitable signature for nuclear forensic purposes in the determination of the origin of uranium material [2]. The suitability is based on the fact that the chemical properties in general are similar for all lanthanides. Therefore, the so called “lanthanide pattern” is considered to be constant throughout the processes of the nuclear fuel cycle, even though the concentration of the lanthanides as a group may be altered. The lanthanide pattern may give an indication of the geographical origin of the uranium ore. Furthermore, lanthanides used as additives later on in the fuel cycle, may give an indication of the uranium production site and/or the intended reactor. Erbium and

gadolinium, for example, are added as burnable poisons, or neutron absorbers, to control the reactivity of the nuclear fuel, especially early-on in the fuel rod life-time.

Mass spectrometry has turned out to be a good technique for measuring the lanthanide series. The technique provides sufficient sensitivity in order to measure dilute amounts of the elements. Even so, mass spectrometric measurements of the lanthanide series are associated with spectral interferences, both isobaric and polyatomic. The isobaric interferences may be avoided, as each of the lanthanides have at least one isotope free from isobars in the lanthanide series. The more difficult task is to avoid or minimize, the polyatomic interferences. Some of the lanthanides, especially the lighter elements, form oxides easily, which will interfere predominantly on the Ln^{16}O^+ mass. Other possible interferences are the formation of hydrides and hydroxides which will be detected at one mass unit above the isotope of interest and at one mass unit above the oxide, respectively. As the lighter elements in the lanthanide series often are present in substantially higher concentrations than the heavier elements, the oxides of the lighter elements may cause major interferences. To measure low levels of lanthanides it may be necessary to chemically remove the uranium from the samples prior to measurement. It is possible to measure the lanthanides with the uranium present, but the high concentration of uranium may cause signal suppression which will decrease the intensity of the analytes, and therefore increase the detection limit.

2.3 OBJECTIVES FOR INTERFERENCE FREE MEASUREMENTS

In this project the requirements for interference free measurements of the lanthanide series have been investigated. The degree of interferences caused by oxides has been quantified for lanthanide containing materials with varying lanthanide patterns. Furthermore, two approaches to solve the problem were evaluated:

- One approach is to use a desolvating sample introduction system during the measurement which removes the solvent, in this case 2% nitric acid, which means that the oxygen needed for oxide formation is removed.
- The other approach is to chemically separate the lanthanides into fractions, such that the interfering and interfered elements are measured in different fractions. Several possible separation procedures have been investigated in the project [3].

2.4 OVERVIEW OF INTERFERENCES

Table 1 shows the interferences in lanthanide measurements caused by isobars and polyatomic species [3]. The isotopes marked in green are fairly straightforward to use for quantification. It is, however, important to make sure that barium has been removed during the separation, as the isotopes and their oxides may interfere with the lighter elements in the lanthanide series. The isotopes marked in red are heavily interfered and should be avoided for quantification, whereas the yellow-marked isotopes may be used but with caution since these masses may be severely interfered depending on the material in question. In order to measure the lanthanides without substantial interferences it would be convenient to divide the series into fractions. In view of Table 1 it would be convenient if the lighter elements, lanthanum to neodymium, are kept in one fraction in order to avoid interferences from those oxides on the middle part elements of the series. Furthermore, interferences from the middle part elements on the heavier elements can similarly be avoided by separating them from each other. Fractioning the elements from samarium to gadolinium has resulted in a straightforward separation procedure, from both the lighter and the heavier elements.

TABLE 1. A SCHEMATIC FIGURE OF THE LANTHANIDE SERIES AND THE INTERFERENCES CAUSED BY ISOBARS AS WELL AS POLYATOMIC SPECIES. THE FIGURES IN THE COLOURED CELLS ARE THE ABUNDANCES OF THE RESPECTIVE ISOTOPES.

m/z	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dv	Ho	Er	Tm	Yb	Lu
136		0.185												
137														
138	0.088	0.251												
139	99.91													
140	¹³⁹ La	88.45												
141		¹⁴⁰ Ce	100											
142		11.11	¹⁴¹ Pr	27.15										
143		¹⁴² Ce		12.17										
144				23.79	3.07									
145				8.293										
146				17.18										
147				¹⁴⁶ Nd	14.99									
148				5.756	11.24									
149				¹⁴⁸ Nd	13.82									
150				5.638	7.38									
151				¹⁵⁰ Nd	¹⁵⁰ Sm	47.81								
152		¹³⁶ Ce			26.75	¹⁵¹ Eu	0.20							
153					¹⁵² Sm	52.19								
154		¹³⁸ Ce			22.75	¹⁵³ Eu	2.18							
155	¹³⁹ La				¹⁵⁴ Sm		14.80							
156	¹³⁹ La	¹⁴⁰ Ce					20.47		0.056					
157		¹⁴⁰ Ce	¹⁴¹ Pr				15.65							
158		¹⁴² Ce	¹⁴¹ Pr	¹⁴² Nd			24.84		0.095					
159		¹⁴² Ce		¹⁴³ Nd			¹⁵⁸ Gd	100						
160				¹⁴⁴ Nd	¹⁴⁴ Sm		21.86	¹⁵⁹ Tb	2.329					
161				¹⁴⁵ Nd	¹⁴⁴ Sm		¹⁶⁰ Gd		18.88					
162				¹⁴⁶ Nd					25.47		0.139			
163				¹⁴⁶ Nd	¹⁴⁷ Sm				24.89					
164				¹⁴⁸ Nd	¹⁴⁸ Sm				28.26		1.601			
165				¹⁴⁸ Nd	¹⁴⁹ Sm				¹⁶⁴ Dv	100				
166				¹⁵⁰ Nd	¹⁵⁰ Sm					¹⁶⁵ Ho	33.50			
167				¹⁵⁰ Nd	¹⁵⁰ Sm	¹⁵¹ Eu					22.86			
168					¹⁵² Sm	¹⁵¹ Eu	¹⁵² Gd				26.97		0.123	
169					¹⁵² Sm	¹⁵³ Eu					¹⁶⁸ Er	100		
170					¹⁵⁴ Sm	¹⁵³ Eu	¹⁵⁴ Gd				14.91	¹⁶⁹ Tm	2.982	
171					¹⁵⁴ Sm		¹⁵⁵ Gd				¹⁷⁰ Er		14.09	
172							¹⁵⁶ Gd		¹⁵⁶ Dv				21.68	
173							¹⁵⁷ Gd		¹⁵⁶ Dv				16.10	
174							¹⁵⁸ Gd		¹⁵⁸ Dv				32.02	
175							¹⁵⁸ Gd	¹⁵⁹ Tb	¹⁵⁸ Dv				¹⁷⁴ Yb	97.40
176							¹⁶⁰ Gd	¹⁵⁹ Tb	¹⁶⁰ Dv				12.99	2.599

2.5 A STUDY ON OXIDE FORMATION RATE

In order to evaluate the oxide formation rate, single element solutions for all lanthanides were measured using an ICP-SFMS, ElementXR, with both a standard (conical spray chamber) and a desolvating (Aridus) sample introduction system. The ratios between isotopes and the corresponding oxides were calculated. The result of the calculated oxide formation for the standard sample introduction system is shown in Table 2. The uncertainties for the measurements vary between 4% and 26% for the lowest ratios, $k=1$. For some of the elements, the hydroxide formation could be quantified, with the highest value for lanthanum at 25 ppm. The hydride formation rate was below the detection limit for all elements.

TABLE 2. CALCULATED LANTHANIDE OXIDE (LnO) FORMATION FOR A STANDARD SAMPLE INTRODUCTION SYSTEM.

LnO Formation (%)

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
5.5	4.2	2.3	2.0	0.22	0.021	1.0	0.77	0.22	0.23	0.23	0.11	0.0072	0.21

The highest significant oxide formation using the desolvating system was 43 ppm for cerium. This means that the oxide formation is approximately a thousand times lower when using a desolvating system than with the standard introduction system. All the other oxide formation rates in the lanthanide series were lower or below detection limit. The stability for the desolvating sample introduction system was significantly lower than for the standard introduction system which will increase measurement uncertainty.

2.6 DEVELOPMENT OF THE SEPARATION METHOD

The proposed method of choice separates the lanthanide elements into three separate fractions; lanthanum to neodymium, samarium to gadolinium and terbium to lutetium. A suitable resin for this kind of sequential elution is Ln-resin. The lanthanides can be eluted in different fractions by increasing the acid concentration in a suitable fashion. In the developed method the lanthanides elute in sequence by increasing the concentration of HCl during the elution. Fig. 1 shows the elution profile from one round of method optimization. The figure shows that it is possible to achieve satisfying separation between the three groups of lanthanides as discussed above.

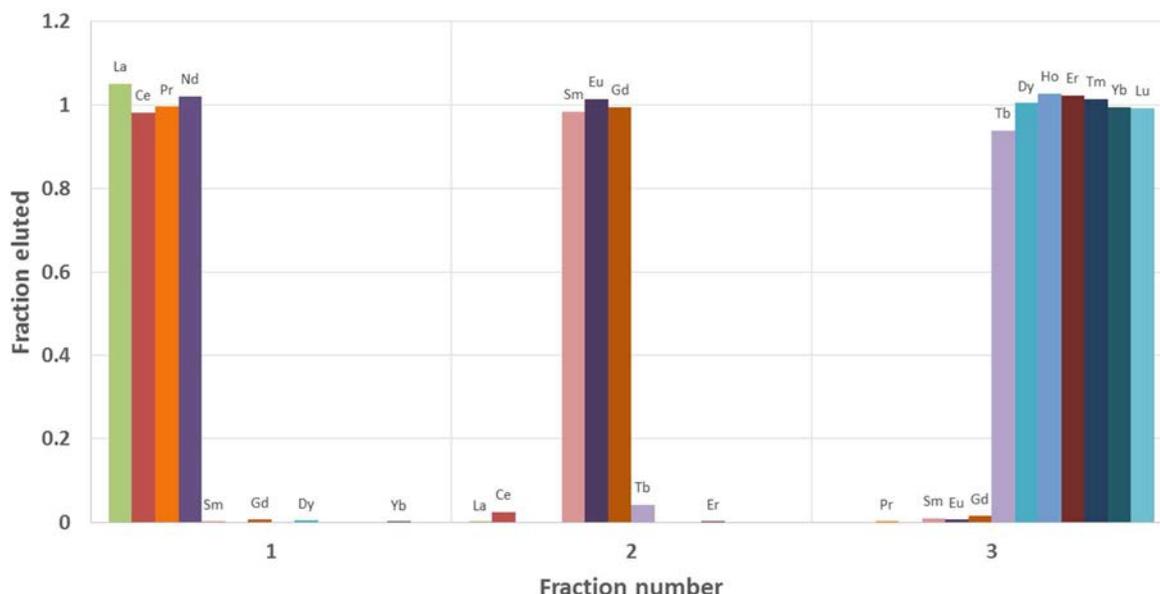


FIG. 1. Elution profile of a chemical separation using Ln resin. The eluent for fractions 1, 2 and 3 consist of 0.4 M HCl, 0.75 M HCl and 8 M HCl, respectively.

2.7 CALCULATION OF INTERFERED VERSUS INTERFERENCE-FREE LANTHANIDE PATTERNS

A reference material certified for lanthanide content, GSS-2 (National Research Center for CRMs, China), was used to illustrate the effect of interferences on the lanthanide pattern and how the attempts to remove the interferences will improve the results. The expected signal from the uncorrected values was calculated by adding the signal from the interfering species to the expected signal of an interference-free measurement. The magnitude of the interference was taken from the oxide formation study above. The interfered lanthanide pattern compared to the pattern using the certified values can be

seen in Fig. 2. It is clear in the figure that both gadolinium and terbium are strongly interfered. In this case the interferences are ^{151}PrO and ^{143}NdO for gadolinium and terbium, respectively. The overestimation of gadolinium is more than 40% for this material.

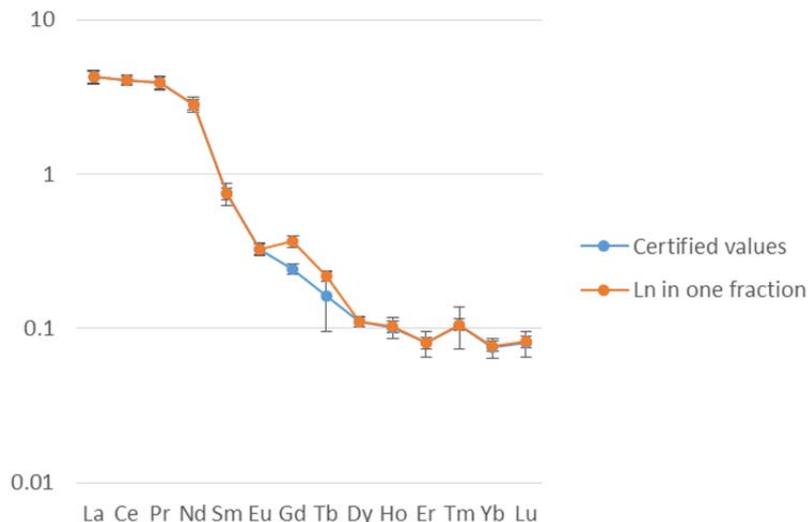


FIG 2. Comparison between certified values and calculated values with lanthanides in one fraction.

If, instead the measurement values are calculated as if the measurements are performed on three separate fractions, the results will correspond to Fig. 3. The correspondence to the certified values is much better in this case. There is only a slight bias of about 2% on lutetium, which originates from ^{159}TbO . This is, however, expected to be within the measurement uncertainty of this method.

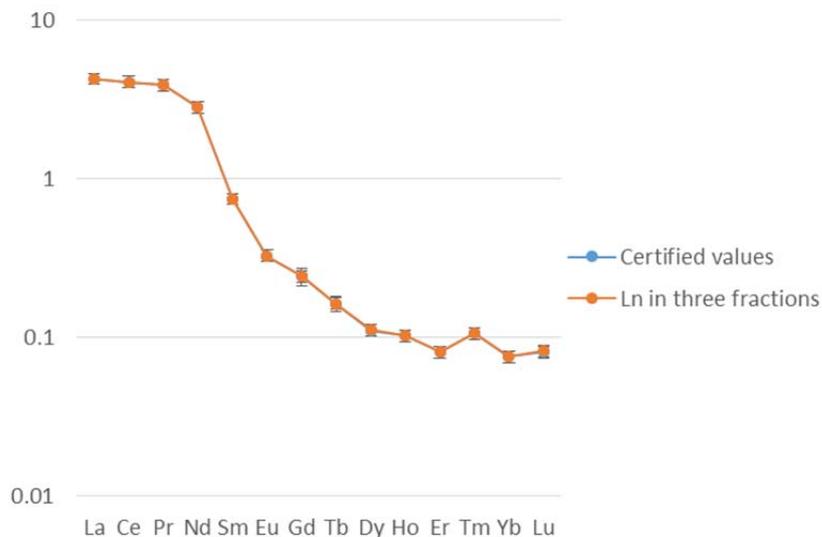


FIG 3. Comparison between certified values and calculated values when the lanthanides are measured in three different fractions.

If, on the other hand, a desolvating sample introduction system is used during measurement the results would correspond with Fig. 4, for measurements on only one fraction for all lanthanides. For this figure the oxide formation is set to 43 ppm, regardless of the element, which is the largest value that was established during the oxide formation rate study with the desolvating system. In reality the oxide formation is lower for most elements. The uncertainty is, however, set at twice the uncertainty for measurements using a standard sample introduction system due to the instability of the signal.

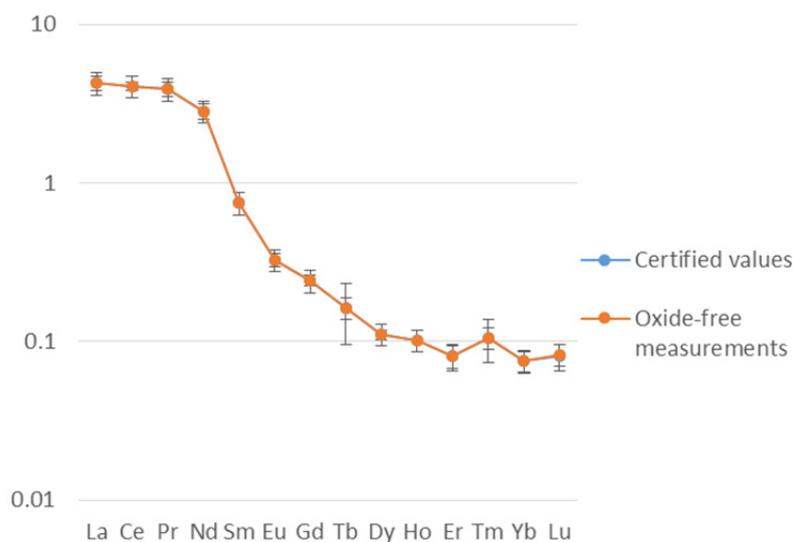


FIG 4. Comparison between certified values and calculated values when a desolvating sample introduction system is used during measurement.

3. CONCLUSIONS

Lanthanide patterns can be an important tool for determination of geographical origin and identification of nuclear material when performing nuclear forensic investigations. However, the nature of the lanthanide series may make them hard to quantify, due to interference problems. The relative concentration between the lighter elements and the heavier elements affects the severity of the interference. For some materials, the interferences may not cause any significant problem but it is important to be aware of the level of oxides in order to make that judgement.

This project presents two approaches to solve this problem. Firstly, by using a sample introduction system that removes the solvent before the sample enters the instrument. This decreases the oxide formation to a level that, in most cases, eliminates the interference problem. The second solution is to separate the lanthanides into fractions in a way that interfering species are separated from analytes. Eluting the elements in three fractions would minimize the interferences but still keep the separation method fairly simple. Both methods deliver reliable results. However, if a desolvating sample introduction system is not readily available to the laboratory, the sequential separation method may be more suitable.

Future work in this area includes further optimization of the separation method and a full validation of the method using certified reference materials.

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RESOLVING NUCLEAR FORENSIC SIGNATURES FROM A URANIUM AND THORIUM MINE IN SOUTH AFRICA USING THE ICP-MS ISOTOPIC RATIO TECHNIQUE

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1. INTRODUCTION

1.1 NUCLEAR FORENSICS AND NUCLEAR SCIENCE

Nuclear forensics is a new branch of nuclear science that has received much attention due to the on-going threat associated with illicit trafficking of nuclear material. Nuclear forensics was “*born*” as a tool to support nuclear security in tracking the origin, trafficking route and intended use of the stolen nuclear or radioactive material [1, 2] and “.....to provide evidence for nuclear attribution” [3]. The objective of nuclear forensics analysis is to identify and document forensic signatures from interdicted nuclear and radiological samples or the surrounding environment.

1.2 NUCLEAR FORENSIC SIGNATURES

There are at least seven stages in the nuclear fuel cycle including: the uranium ore body underground, the milling and processing of the ore, conversion to the yellow cake, enrichment of uranium in ^{235}U , nuclear reactor operation, the spent fuel (nuclear waste) stage and the re-processing of spent fuel [4, 5]. Every stage of the nuclear fuel cycle has nuclear signatures, however in this work we focus on the first two stages.

Uranium (or gold) ores possess characteristic signatures according to the geology of the bedrock [6]. Mining and processing of uranium and thorium leaves behind distinctive signatures that identify the mining area (e.g. shaft) and the chemical processing used [4].

2. WORK CONDUCTED

2.1 OBJECTIVE OF THE STUDY

The objective of this work is to demonstrate the use of the inductively coupled plasma - mass spectrometry (ICP-MS) isotopic ratio technique as a viable tool for resolving nuclear forensic signatures from a uranium/thorium mine in South Africa. Results from the first stage in the fuel cycle are described here, and the data presented could form a basis for a South African nuclear forensics library. However a comprehensive nuclear forensic library can only be developed when all the stages in the fuel cycle have been investigated.

2.2 STUDY AREA

An aerial photograph of the study area is provided in Fig. 1; the authors cannot give further details due to confidentiality agreements.

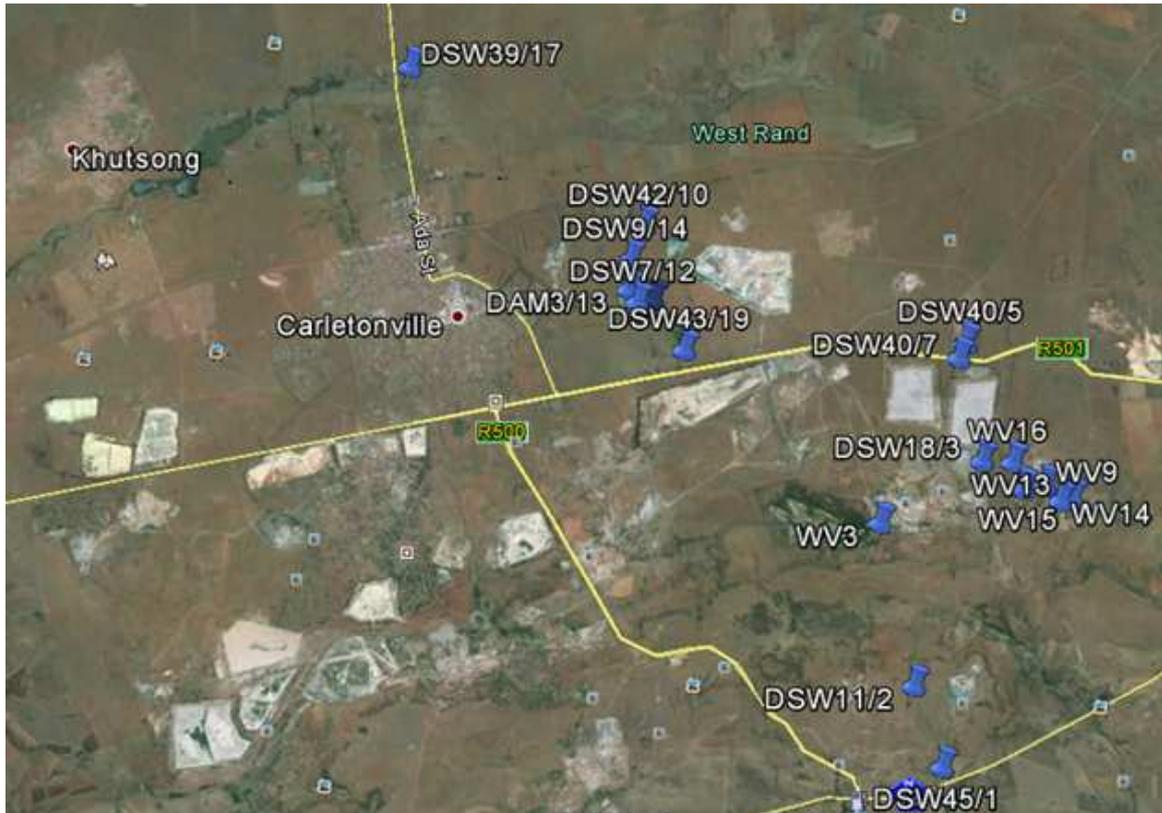


FIG. 1. Aerial photograph of water sampling points in the Carletonville goldfields Area of South Africa. From the top of this figure: DSW39/17- Water from DSW36/15 and DSW38/16; DSW36/15- Water from DSW9/14 and DSW42/10); DSW38/16- Discharge water from another mine; DSW42/10- Fissure water straight from underground; DSW9/14-Water from the settling point; DSW7/12-Water coming from the mine shaft and from process plants; DAM3/13-Water after (downstream of) the settling point; DSW43/19-Purified water; DSW40/5 & DSW40/7- Raw water from return water dam; DSW18/3 & DSW112-Sewage water from mine shaft; DSW45/1- water from mine shaft; WV16, WV9, WV13, WV14, WV15 & WV3- Borehole water for public use from West village.

2.3 EXPERIMENTAL METHODS

2.3.1 Sample collection and preparation

The samples used in this study consisted of a mixture of mine water (also called *fissure* water from underground at the ore deposits) used to cool the drilling machine, waste water from the processing plant and soil samples from the mine tailing. It was observed that the slurry from the plant is deposited on the tailing dam in paddocks. Fig 2 shows an example of an active (functional) tailing and a disused tailing. The soil and some water samples were collected from the top of each tailing and the discharge canals respectively to represent uranium that has come from the milling and processing stage of the fuel cycle. Fissure water samples were also collected from the mine shafts outlets to represents uranium from the ore body.

2.3.2 Instrumentation

The spectrometric analysis was carried out using the Perkin Elmer ICP-MS 300Q equipped with dual detectors. Soil, and water samples were digested using a Multiwave 3000, Anton Paar microwave oven manufactured by Perkin Elmer, according the aqua regia method [7]. The reagents used were of Suprapur analytical grade (by Merk, Darmstadt, Germany). All digested sampled were then preserved at 4°C for later analysis in the laboratory



FIG. 2: Aerial photographs; on the left is the tailing dam showing the paddocks and on the right is the disused tailing dam. Yellow marks represent sampling points.

2.3.3 ICP-MS calibration

Procedures supplied by the manufacturer were used to calibrate the Perkin Elmer®, NeXION 300Q, inductively coupled plasma mass spectrometer (ICP-MS). For the total quantitative method, the standards have 10 milligrams per litre of Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U and Zn [8].

For the isotope ratio method, the instrument uses the ^{107}Ag and ^{109}Ag isotopes as the calibration standards with the same concentrations. The mass abundance of silver isotopic standard is shown in Table 2.

2.4 RESULTS AND DISCUSSION

TABLE 1. SUMMARY OF ISOTOPIC RATIOS FOR A PARTICULAR SET OF SAMPLES CODED 1075 IN THE STUDY AREA.

		Samples 1075 from Tailings dams		Sample <i>Fissure</i> Mine water	
Analyte	Mass.	Net Intensity	Mass Frac. Mean ($\mu\text{gL}^{-1}\pm 1\sigma$)	Net Intensity	Mass Frac. Mean ($\mu\text{gL}^{-1}\pm 1\sigma$)
Ag	107	1149.7	0.07562	6.2	0.09873
Ag	109	884.0	0.92438	6.3	0.90127
Sr	84	1589.1	1.00000	204.1	1.00000
Rb	85	38923.3	1.00000	1277.8	1.00000
Co	59	806760.8	1.00000	2408.2	1.00000
Ni	58	[13762252.3]	1.00000	7327.1	1.00000
Pa	231	0.9	1.00000	0.1	1.00000
Th	232	84043.3	1.00000	10.2	1.00000
Bi	209	8668.1	1.00000	-9.0	1.00000
Pb	204	4487.3	0.00046	10.5	0.01418
Pb	206	9262494.7	0.96781	187.0	0.25622
Pb	207	132098.9	0.01386	153.8	0.21178
Pb	208	169396.6	0.01787	374.5	0.51781
U	234	21.3	0.00000	0.2	0.00008
U	235	3043.4	0.00042	17.8	0.00713
U	238	200167.6	0.99958	2436.9	0.99279

Table 1 reveals the following characteristics of the mine. For the tailings dam samples, the isotopic concentrations of the U isotopes varied widely from one sample to the other however most of the samples from *fissure* water had very close isotopic concentration of U isotopes. An example is given in the Table 1 above in the last four columns for both cases. The concentration of ^{235}U in the *fissure* water shows that this sample is natural uranium before extraction by chemical processes, while that from the tailing has very low ^{235}U . This in itself is a signature that distinguishes between ore uranium and processed uranium for the South African mine investigated. For this mine too, the concentration of ^{206}Pb is unexpectedly high signifying ore deposits rich in ^{238}U . Even the intensity levels of the samples at the two stages of the fuel cycle (mining and processing) are also different.

From Fig. 3, all samples show a strong positive Tb anomaly indicating no fractionation of heavy rare earth (HREE: Tb–Lu). Probably this is due to geotectonic activity associated with the Witwatersrand area (Orkney earthquake of 2014). The seismic instability might be causing hydrothermal enrichment of Tb. The other HREE with atomic numbers greater than Er were all below the detection limit of our ICP-MS. Light rare earth (LREE: La – Gd) are relatively flat showing that they were not changed by uranium processing nor geological factors in the earthquake prone mining area. However, the LREE do show small negative Nd anomaly and a very slight enrichment of Ce. Enrichment of Ce is a signature which can be explained to mean that the so called LREE comprising Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd (sometimes described as the cerium group) are dominant in this gold/uranium ore body. The HREE comprising Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu (also described as the yttrium group) are of negligible concentrations [9, 10]. We can use the proportions of these REE for geochronology and fossil date since their concentrations in rocks are only slowly changed by geochemical processes. This will be part of the second phase of this project.

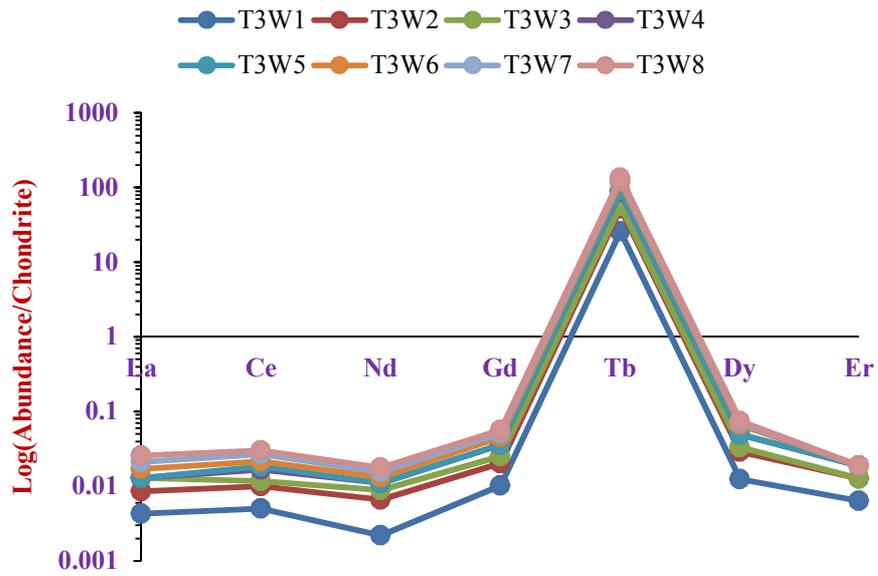


FIG 3. Chondrite normalized lanthanide (REE) patterns for tailing dam 3.

In Fig. 4, lead isotope ratios for mine (fissure) waters collected from this South African gold mine have $^{207}\text{Pb}/^{204}\text{Pb}$ values distinctively ranging from about $12 \mu\text{gL}^{-1}$ to $18.5 \mu\text{gL}^{-1}$. This is distinctively different from lead samples in UK, Germany, Poland, Italy, and Spain [4]. Fig. 5 represents lead isotope ratios determined from tailing samples.

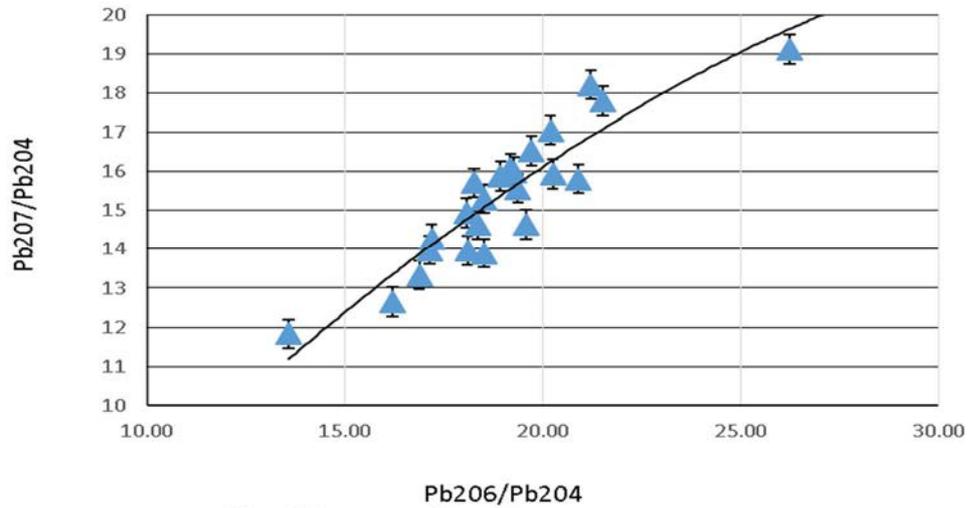


FIG. 4. A plot $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for mine (fissure) water samples.

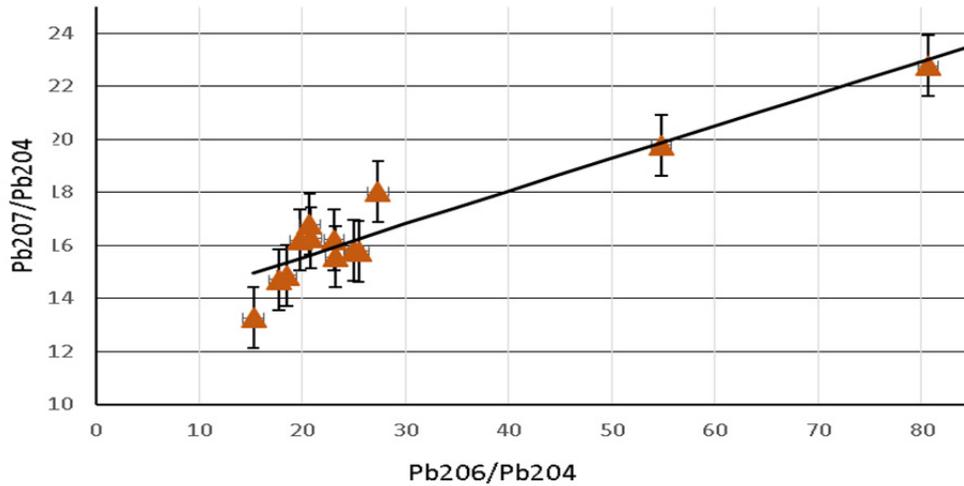


FIG 5. A plot of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for tailing samples.

Comparing Fig 4 and Fig 5, it is evident that the signature for uranium in the mine (fissure) water, which contains uranium from the ore, is distinctly different from that for uranium in a tailing dam which has undergone various processing techniques. Both the vertical and horizontal ranges are different, with the last two points in Fig. 5 seemingly outliers. A close examination of the isotopes indicates that these two points reflect a higher value of ^{206}Pb (implying higher ^{238}U concentration) and a lower value of ^{204}Pb implying these two deposits are of radiogenic origin [11].

The characteristic difference between Fig. 6 and Fig. 7 signatures is quite striking. Fig 6 reflects the geographical origin of a nuclear material while Fig. 7 is indicative of the geological origin of the deposit (radiogenic in this case). Again both vertical and horizontal scales are different. No polynomial fit could be assigned to the Fig. 6 data plot.

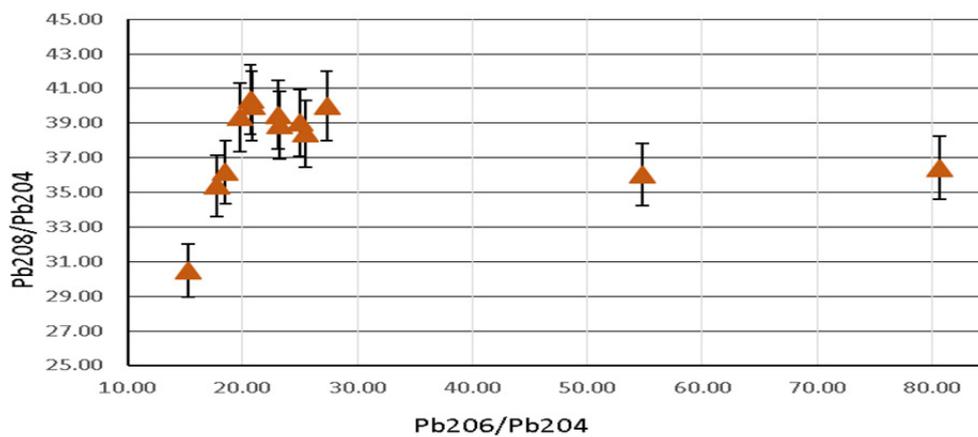


FIG 6. Variation of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for tailing samples.

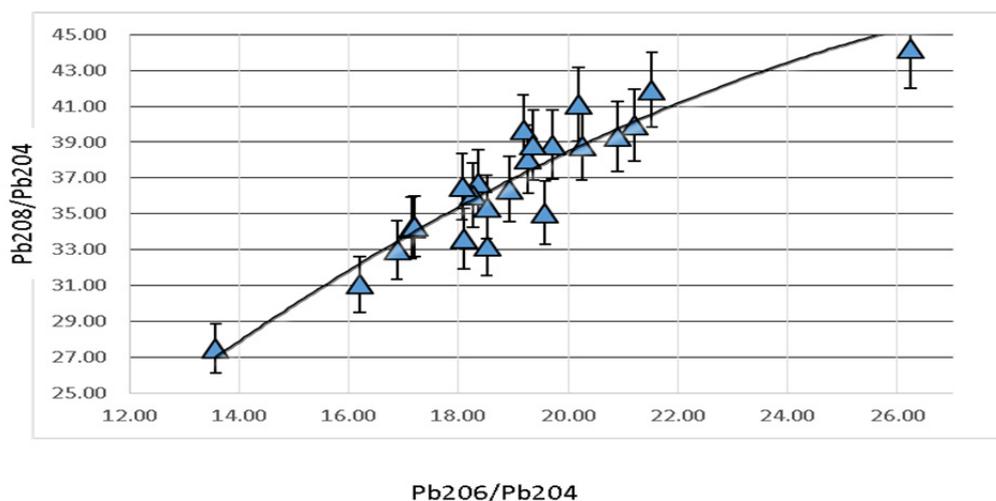


FIG 7. $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for mine (fissure) water samples.

3. CONCLUSIONS

This work has demonstrated the viability of the ICP-MS isotopic ratio method as a technique for developing nuclear forensics signatures for a South African uranium mine. The nuclear forensic graphs presented here provide enough evidence to confirm that uranium ore signatures are significantly different from processed uranium signatures. The former indicate the geochemical origins of an interdicted sample, while the later points to the geographical origin. Ore samples were shown to contain balanced isotopic ratios of ^{238}U , ^{235}U and ^{234}U , while tailing samples revealed a depletion of these ratios maybe due to modern processing techniques. The uranium, possibly embedded in phosphorite deposit in apatite and fluorapatite minerals, is recovered from phosphoric acid leaching followed by lime precipitation to remove impurities and magnesia is used for precipitation of the uranium. There is however, a need to expand this work to at least ten more mines with a wider geographical area in South Africa and also to verify these results using other techniques like TIMS or XRF. The researchers therefore will continue this investigation with samples from other mines and then follow each stage of the fuel cycle unto the uranium waste samples (spent fuel from the South African reactors). It is hoped that in a few years' time South Africa will have a reliable nuclear forensics library for attribution and to support criminal prosecutions.

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RESEARCH REPORTS FROM THE RUSSIAN FEDERATION

Following are three reports summarizing nuclear forensic research conducted by leading institutes in the Russian Federation. By design these reports represent individual funded research contracts with the IAEA. The research undertaken was not included as part of the CRP J02003, but rather utilized the unique capabilities, infrastructure and scientific expertise of the Russian institutes.

1. THREE RESEARCH TITLES

“Development of Techniques for Detection and Subsequent Analysis of Alpha-Emitting Microparticles on Fabrics” conducted by the Laboratory for Microparticle Analysis.

“Development of a Gamma-Spectrometric Procedure for the Identification of Uranium and Plutonium in the Presence of Gamma-Emitting Radionuclide Markers Indicative of Spent Nuclear Fuel (SNF) out of Regulatory Control” conducted by the Joint Stock Company ‘V.G. Khlopin Radium Institute’.

“Development of the Trace Element Technique for the Measurement of the Characteristic Impurities of U_3O_8 for Identification Purposes in the Illicit Trafficking of Nuclear Materials” conducted by the A.A. Bochvar High Technology Research Institute of Inorganic Materials (SC ‘VNIINM’).

DEVELOPMENT OF TECHNIQUES FOR DETECTION AND SUBSEQUENT ANALYSIS OF ALPHA-EMITTING MICROPARTICLES ON FABRICS

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1. INTRODUCTION

The purpose of this report is to present the results of research work that was carried out under the IAEA Technical Contract No. 17860. Detection of rare uranium and plutonium microparticles on the surfaces of different textile objects and determination of whether the source of the alpha-emitting microparticles is uranium, plutonium or other alpha-emitting isotopes can be crucial for full-scale investigation of some incidents involving nuclear and radioactive material out of regulatory control. Detection of alpha-emitting particles and determination of the particle composition including uranium, plutonium or other alpha-emitting isotopes are based on the results of analysis of the orientation and shape of tracks caused by the impact of alpha particles in a polycarbonate detector. Moreover the number of tracks allows an estimation of the amount of uranium and/or plutonium in the microparticle and consequently an estimation of the particle size.

Alpha autoradiography allows only preliminary information concerning microparticle characteristics. Therefore further investigation of interesting microparticles by using more precise electron beam and ion beam techniques or inductively coupled plasma mass spectrometry (ICP-MS) analytical methods may be necessary. As a rule, unique alpha-emitting microparticles cannot be analyzed using high sensitive microbeam methods if such a particle is located on the surface of electrically nonconductive clothing and other fabrics. Individual microparticles cannot be analyzed on the textile surface correctly by ICP-MS also because other microparticles will be dissolved together with particle of interest during sample preparation. Therefore, extraction of particles of interest from bearing objects is a necessary preliminary step before very advanced and in-depth analyses. Appropriate procedures should be included in the capability of nuclear forensic laboratories.

Preliminary information about the nature of microparticle alpha emissions, that is, whether they are associated with uranium, plutonium or other alpha-emitting isotopes, can help inform a decision whether to analyze detected alpha-emitting microparticle more precisely or not. Extraction of an alpha-emitting microparticle from fabric surface for further analysis is very labor intensive, and it is expedient only if such further analysis will provide additional useful information in support of a law enforcement investigation

There are various options for further analysis of microparticles after their removal from fabric. In this research work the following possibilities are considered: determination of isotope ratios of plutonium in microparticles using secondary ion mass spectrometry (SIMS), determination of the production date of plutonium in microparticles using SIMS and ICP-MS, and the measurement of trace elements using ICP-MS.

2. WORK CONDUCTED

2.1 ALPHA TRACK PARAMETERS AND THE COMPOSITION OF URANIUM AND PLUTONIUM IN ANALYZED MICROPARTICLES

Alpha track detectors TASTRAK CR-39 (Track Analysis Systems Limited, UK) were used for registration of alpha particles in this work. The typical track of an alpha particle impinging the detector at an acute angle to its surface is shown in Fig. 1.

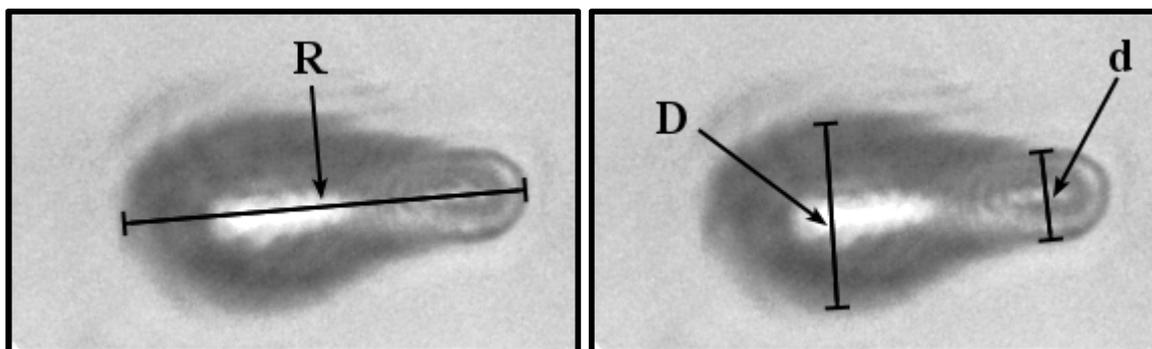


FIG. 1. Parameters of individual alpha-track: length (large axis) R , diameter D of the input hole, diameter d of the curvature of cone top of the track.

For registration of alpha tracks in this work, the detectors were set at a distance about 200 μm above the surface being investigated.

Clusters of tracks from uranium particles and from plutonium particles as well as from particles which contain both were investigated for the experimental confirmation of validity of the suggested approach. The microparticles of uranium and plutonium were not monoisotopic. Uranium was enriched above 20at% ^{235}U (HEU). The main alpha-emitter of that material is ^{234}U . This isotope emits alpha-particles with an energy of about 4.8 MeV. The yield of alpha particles from ^{235}U with an energy of about 4.4 MeV is on the order of several percent. The yield of alpha particles from ^{238}U may be less than 1%.

Plutonium-239 and ^{240}Pu are the main isotopes of the plutonium used in these experiments. These isotopes provided alpha particles with energies of approximately 5.15 MeV. Minor, but much more radioactive isotopes of ^{238}Pu and ^{241}Am provide no more than 20% of alpha particles; the energies of these alpha particles are about 5.5 MeV.

2.2 DISTINGUISHING ALPHA TRACKS FROM URANIUM AND FROM PLUTONIUM MICROPARTICLES

The shape and size characteristics of the alpha particle tracks are functions of the energy of the emitted alpha particle [1, 2]. The study of the alpha-track geometry from thin layers of ^{235}U , ^{239}Pu and ^{241}Am indicate that among all geometry parameters diameter (d) of the curvature of cone top of the track is most dependent on the energy of the alpha particle [2]. Therefore the diameter (d) was measured in this work for characterization of alpha-emitting isotopes.

Energies of alpha particles of some uranium and plutonium isotopes and ^{241}Am as well as parameters of size distribution of the curvature of corresponding cone tops are presented in Table 1. These parameters provide information on the size distributions of the curvature of the track cone tops that can resolve the alpha emissions of different isotopes. The measurements of track geometry parameters in this work were implemented according to the developed technique [3].

TABLE 1. ENERGIES OF ALPHA PARTICLES AND PARAMETERS OF SIZE DISTRIBUTION OF DIAMETER (d)

Isotope	^{235}U	^{234}U	$^{239}\text{Pu} + ^{240}\text{Pu}$	$^{238}\text{Pu} + ^{241}\text{Am}$
E_{α} , MeV	4.4	4.8	5.15	5.5
Average d_{av} , μm	11.5	8.8	6	3.6
Std. deviation σ , μm	0.7	0.7	0.8	0.5

Images of typical small uranium and plutonium particles, track clusters, as well as corresponding histograms of track distributions geometry (d values) of four similar uranium particles and two similar plutonium particles are presented in Fig. 2.

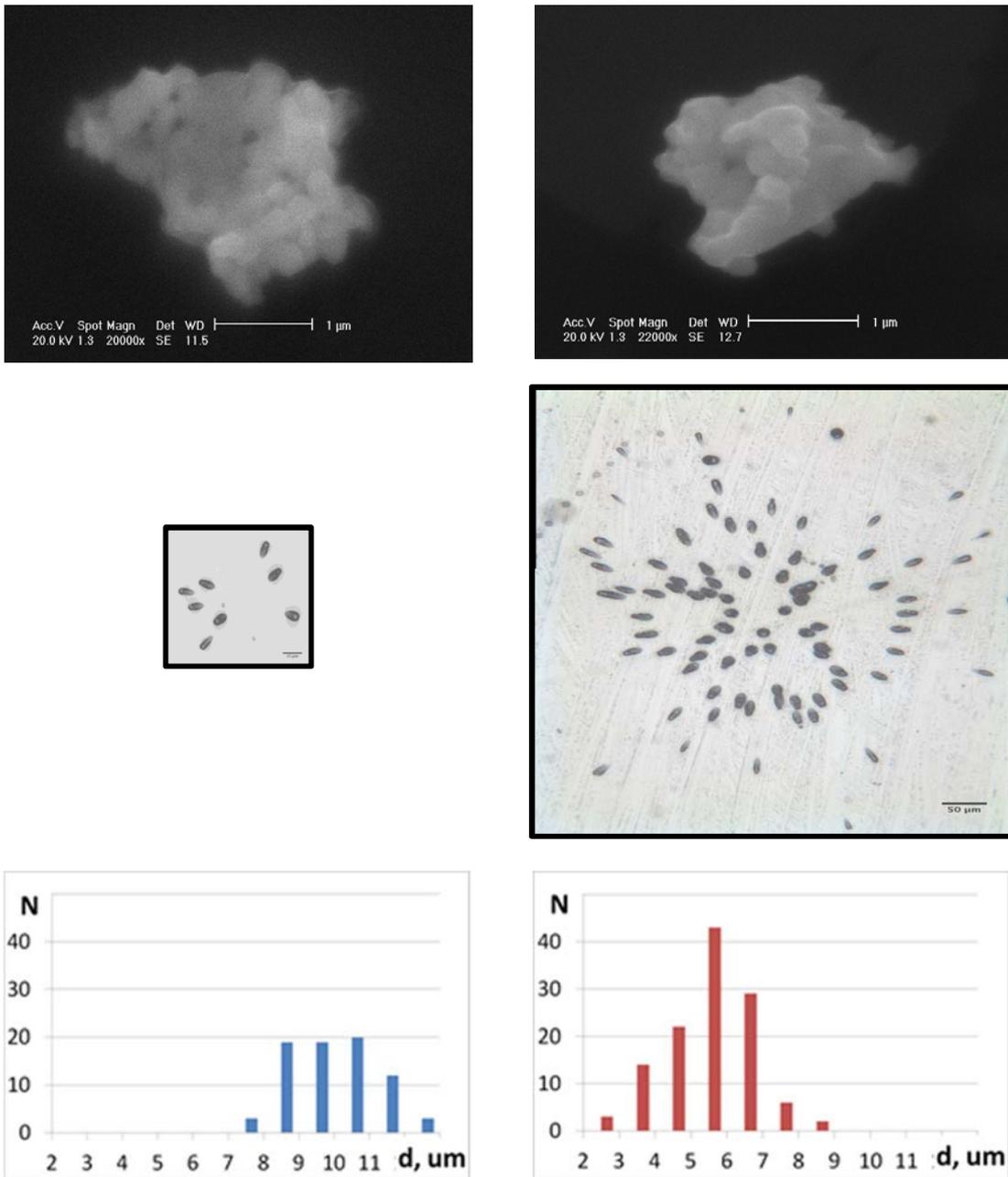


FIG. 2. Uranium (left) and plutonium (right) particles, corresponding alpha tracks clusters and histograms of tracks distribution on d values for 4 uranium particles (blue) and 2 plutonium particles (red).

Tracks from several similar particles were processed to provide acceptable statistics. Comparison of the histograms for uranium and for plutonium particles allows the conclusion that alpha autoradiography of examined objects can provide information not only about the location of alpha-emitting microparticles on the surface of an object, but also whether the particle is HEU or plutonium or another alpha-emitting isotope. Of course, to note, alpha autoradiography cannot distinguish isotopes which emit alpha particles with similar energies.

2.3 DETECTION AND EXTRACTION OF ALPHA-EMITTING MICROPARTICLES

Microparticles of HEU and microparticles of a mixture of HEU and plutonium were used for validation of the developed techniques. Special samples were prepared by putting these microparticles on the surface of cotton fabric. The fabric surface was wetted by a 0.4% solution of polyisobutylene in heptane to fix particles on the surface.

The track detectors above the sample were exposed for 48 hours. Such duration provides registration of tracks from HEU particles with sizes of about 2 μm and of tracks from plutonium particles of a size about 0.2 μm and greater. Exposed detectors were etched in 6M solution of NaOH for 4 hours at 80°C. Clusters of the developed tracks were used for characterization of particles.

Prolongation of the axis R of the track reconstructs the projection of the trajectory of the alpha-particle, emitted from the surface of the alpha-emitting microparticle onto the detector plane. The origin of several radial prolongations of tracks of the same cluster provides information on the location of the microparticle on the surface of the investigated object. Fig. 3 illustrates the process of determination of the area of the radial tracks and the localization of the emitting particle.

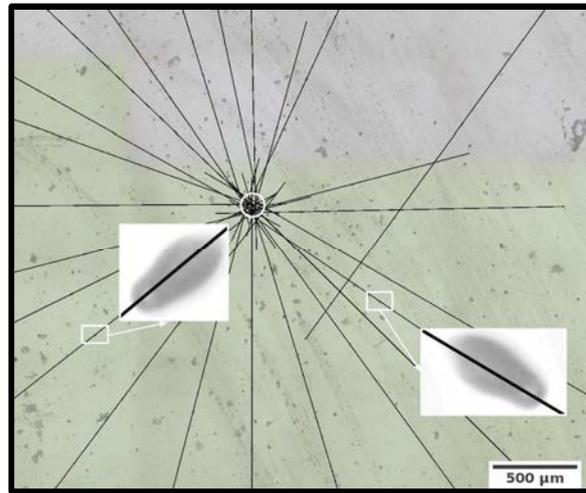


FIG. 3. Determination of the center of alpha tracks cluster.

A specially manufactured template with coordinated grid is used to correct the re-alignment of developed detector and the analyzed sample. The use of this template allows the localization of particles on the fabric surface with an uncertainty about 150 to 200 μm . A punch was manufactured for circular cutting of the fabric fragments which contain alpha-emitting microparticles. The diameter of the cut fragment is 5 mm (Fig. 4). This size guarantees the presence of the microparticle on the cut piece of fabric and provides for convenient further manipulation of the fragment. The presence of microparticles on the cut fragments is confirmed by the results of the exposure of alpha track detectors over these cut fragments.

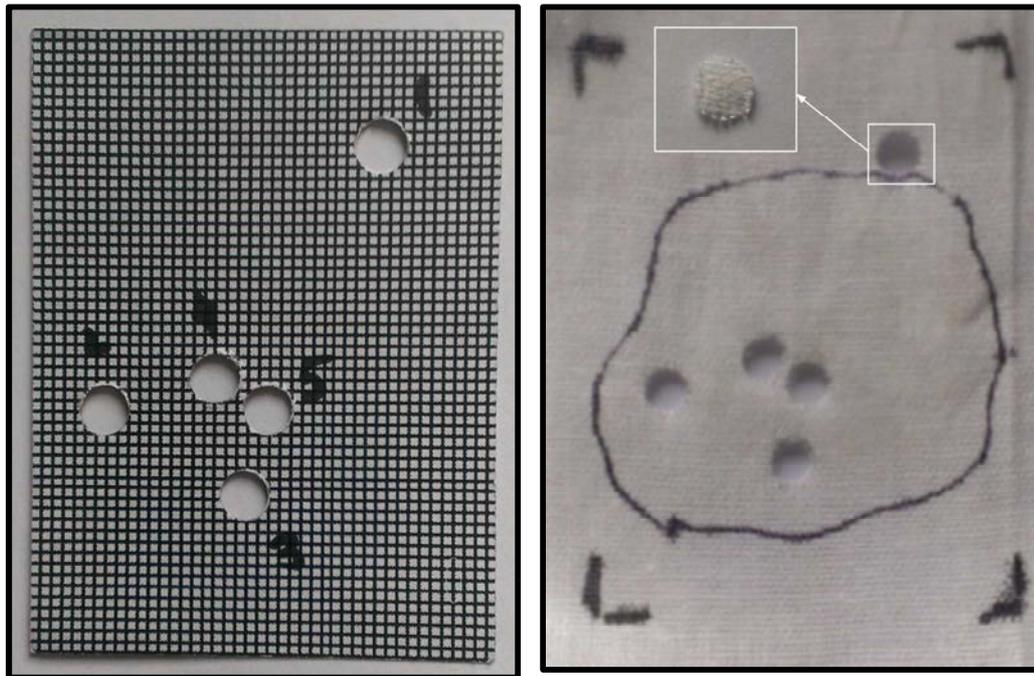


FIG. 4. Girded template (left) and fabric (right) with one cut fragment (the size has been slightly increased). Five holes from 5 cut fragments can be seen also on fabric surface.

2.4 INFORMATION ABOUT COMPOSITION AND SIZE OF ALPHA-EMITTING MICROPARTICLES

Preliminary information about the composition and size of alpha-emitting microparticles is important particularly if it is not possible to conduct a comprehensive microanalytical examination of all microparticles. The possibility of obtaining relevant preliminary information was checked in this work by comparing the results of alpha autoradiography with the results of ICP-MS of two cut fragments (one of them is shown in Fig. 4). ICP-MS was utilized for much more accurate measurement of amount of the uranium and plutonium in these fragments (analyzing two microparticles with different elemental compositions) and for confirmation of the alpha autoradiography results. Distribution of tracks for diameter d for particle 1 is shown in Fig. 5.

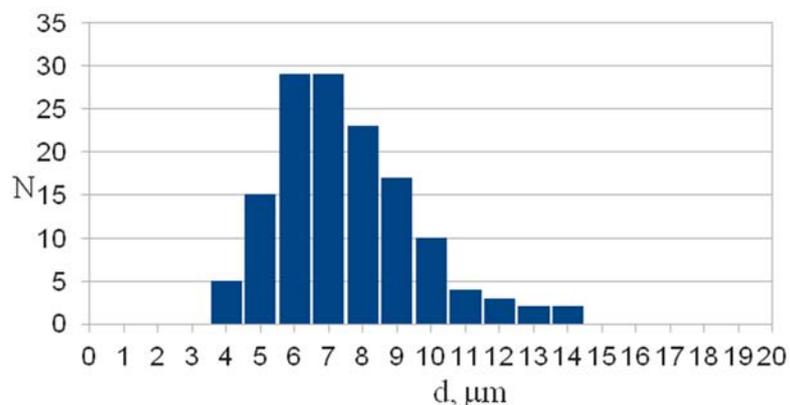


FIG. 5. Distribution of tracks for diameter d for particle 1 taken from fragment 1.

The total number of tracks is 347. The distribution maximum of about $d = 6 \mu\text{m}$ confirms the presence of plutonium. Generally speaking, expanding the size distribution to the direction of the larger d values can be caused by the presence of uranium as well as by a relatively large size of the plutonium

microparticles with commensurate number of alpha particles which have lost energy inside the solid microparticle.

The total amount of tracks and the alpha radioactivity of particle 1 does not correspond to a relatively large plutonium microparticle. It corresponds to a spherical plutonium particle with a diameter about 0.5 μm . No energy loss can be noted under such size. Therefore it may be concluded that both plutonium and HEU are present in this microparticle. Tracks with a d value = 14 μm can be formed by alpha particles emitted by the ^{234}U nucleus with a corresponding trajectory of about 3 μm inside the solid microparticle.

Amounts of plutonium and HEU in a microparticle can be estimated by dividing the size distribution of d in correspondence with two modeling size distributions: i) a common distribution for ^{239}Pu and ^{240}Pu and ii) a distribution for ^{234}U . Selecting the distribution maximums, summarizing these modeling distributions and inscribing the sum of two modeling distributions into an experimental distribution allows for the derivation of approximate distributions. Two such distributions for particle 1 are shown in Fig. 6.

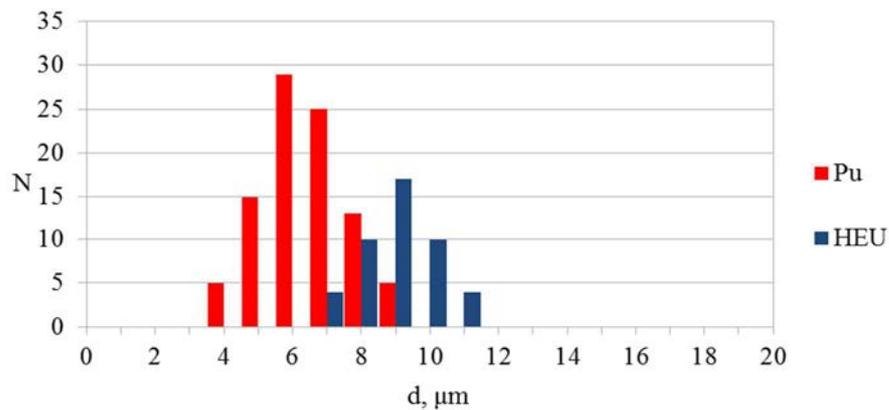


Fig. 6. Dividing of distribution of fig. 5 on two modeling distributions: “ $^{239}\text{Pu} + ^{240}\text{Pu}$ distribution” (red) and “ ^{234}U -distribution” (blue).

This division of the total amount of tracks determines that the size of the spherical HEU oxide particle is about 3 μm and the size of the spherical plutonium oxide particle is about 0.5 μm . It means that the size of the single particle is about 3 μm . ICP-MS results confirm the presence of both plutonium and HEU in this microparticle. Measured amounts of plutonium and uranium correspond to spherical microparticles of plutonium oxide with a diameter of 0.51 μm and spherical microparticle of HEU oxide with a diameter of 2.6 μm . The ICP-MS results confirm the approximate estimation of microparticle size using alpha autoradiography.

The size distributions of the alpha radiography d value diameters for particle 2 are presented in Fig. 7.

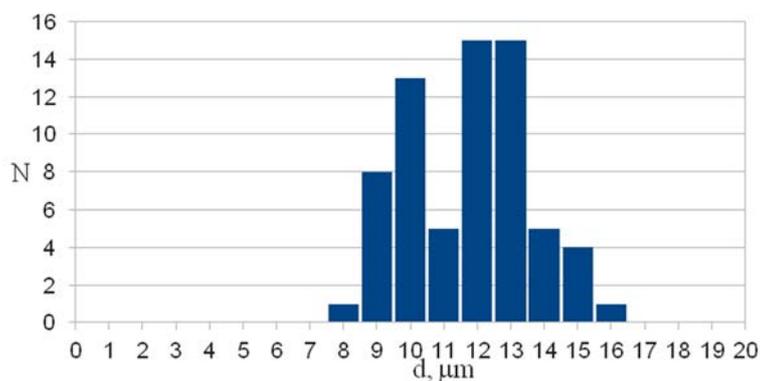


FIG. 7. Distribution of track diameter d values for fragment 2 (particle 2).

The total number of tracks is 183 which provide worse statistics in comparison with particle 1. The minimum diameter d is about $8\ \mu\text{m}$. This result means that the microparticle does not contain plutonium and contains HEU only. The maximum diameter d is about $16\ \mu\text{m}$. The trajectory is about $6\ \mu\text{m}$ inside the solid of the microparticle for an alpha particle emitted from the nucleus of ^{234}U . The track sizes correspond to the size of HEU oxide microparticles.

ICP-MS results confirm the sole presence of HEU in this microparticle. The measured amount of HEU corresponds to a spherical microparticle of HEU oxide with diameter $7.2\ \mu\text{m}$, which is relatively close to the $6\ \mu\text{m}$ determined by the alpha autoradiography method.

2.5 DISMANTLING OF THE FABRIC FRAGMENT INTO INDIVIDUAL FIBERS

In spite of the importance of preliminary information which can be obtained by alpha autoradiography this information may be not enough to meet the minimum prosecutorial requirement, and further analysis of rare alpha-emitting microparticles using more sophisticated methods may be necessary. Microparticles of interest should be removed from fabric for such an investigation. The most reliable technique for removing a microparticle is by dismantling a cut fragment. Either the alpha-emitting microparticle will fall off from the fabric on the substrate surface during dismantling or one fiber with an imbedded alpha-emitting microparticle will be separated.

Dismantling of the fabric fragment into individual fibers is carried out in two stages. The first stage is the dismantling of the fabric fragment into individual threads. This is illustrated in Fig. 8.

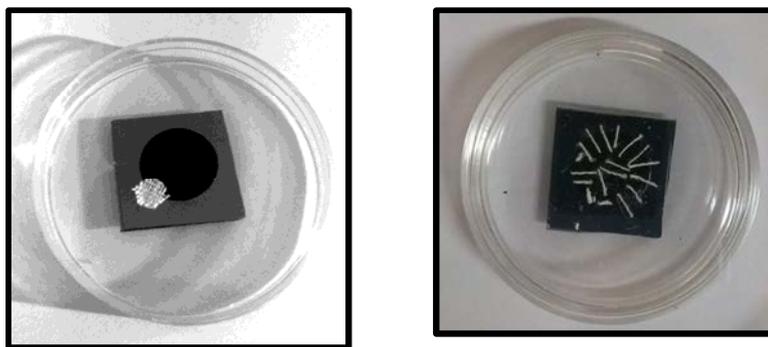


FIG. 8. Dismantling of the fiber fragment into individual threads.
Left – whole fragment before dismantling; right – individual threads after dismantling.

If the alpha-emitting microparticle was not broken away from the fragment or from its threads and was not dropped onto the substrate during the first stage, further processing is required. The second stage involves dismantling of thread which contains an alpha-emitting microparticle into individual

fibers. Following this, the thread, which contains this alpha-emitting microparticle, should be analyzed after dismantling of the fragment into individual threads using alpha autoradiography.

The second stage of dismantling is illustrated by Fig. 9. After identification of a target fiber which bears an alpha-emitting microparticle, localization of this microparticle on the surface of the fiber can be made by using a fabricated holder. This holder provides repeat superposition of the sample on the track detector after its exposure with a shift of no more than 3 μm .

Prior investigation of individual fibers confirms that microparticles on the surface of individual fibers can be analyzed by electron beam and ion beam methods despite the non-conductivity of fibers. Therefore information about alpha-emitting microparticles can be obtained by these methods even if the microparticle is located on the surface of an individual fiber and unlike the situation when microparticles are located on the surface of intact fabric.

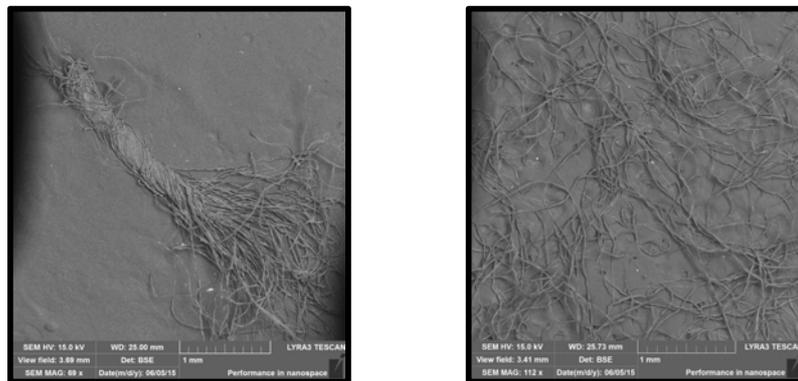


FIG. 9. Dismantling of thread into the individual fibers.
Left – whole thread before dismantling; right – individual fiber after dismantling.

2.6 FURTHER ANALYSIS OF ALPHA-EMITTING MICROPARTICLES, EXTRACTED FROM FABRICS

Further analysis of microparticles which are removed from fabric is undertaken in the same manner as the investigation of any microparticle that is located on the solid conductive substrate. The following analyses are carried out in the frame of this research work: i) isotopic analysis of plutonium in microparticles, ii) determination of the production date of plutonium (“age”) and iii) trace elements analysis. The accuracy of the plutonium isotopic composition, measured by a Cameca IMS-1280 mass spectrometer is illustrated in Fig. 10.

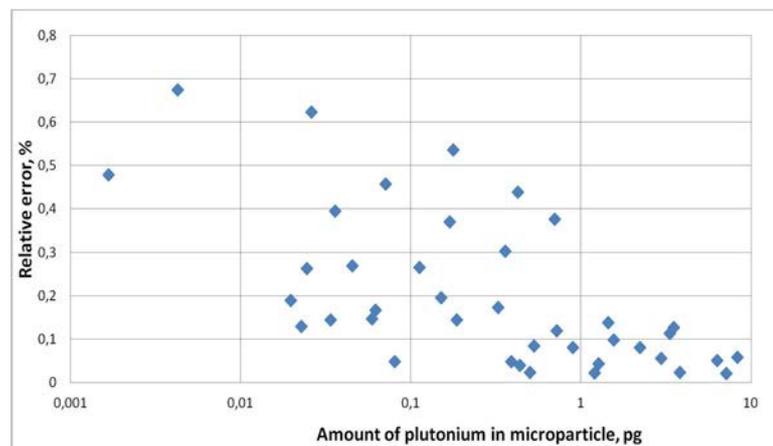


FIG. 10. Relative errors of plutonium isotopes contents, measured by secondary ion mass spectrometry (Cameca IMS-1280).

The data allows for the estimation of uncertainties in the isotopic analysis of plutonium of any isotopic composition. For example concentrations of ^{239}Pu and ^{240}Pu in microparticles with sizes of about $1\ \mu\text{m}$ from nuclear fuel pellets for RBMK reactors (as a rule these concentrations are from 30% to 60%) can be measured with uncertainties from 0.03% to approximately 1%.

The “age” of plutonium is determined by the ratio of daughter to parent isotopes: $^{235}\text{U}/^{239}\text{Pu}$ and $^{236}\text{U}/^{240}\text{Pu}$. Of course, the results of such determination may be valid only if the uranium daughter was not present in original material. Therefore before any measurement of the “age” of plutonium in microparticles it is necessary to be sure that uranium is not present in the original material. Such assurance in this research work was provided by wavelength dispersive electron microprobe analysis of the microparticles. A wavelength dispersive x ray detector was used for the microanalyses, due to much higher resolution of spectra and accordingly lower detection limits for uranium in comparison with an x ray energy dispersive detector. The concentration of uranium in the material is lower than 0.05%; this result allows for the conclusion that uranium was not a component of the original plutonium oxide material.

A Cameca IMS-4F secondary ion mass spectrometer was used for plutonium dating . Mass spectra in the range of 230 to 245 atomic mass units which were obtained for three analyzed particles. Table 2 provides isotopic ratios of $^{235}\text{U}/^{239}\text{Pu}$ and $^{236}\text{U}/^{240}\text{Pu}$ and the corresponding plutonium age calculation using equal coefficients for the ionization for uranium and for plutonium.

TABLE 2. ESTIMATED VALUES OF THE “AGE” FOR PLUTONIUM IN MICROPARTICLES

Particle ID	$^{235}\text{U}/^{239}\text{Pu}, \times 10^{-3}$	“Age”, years	$^{236}\text{U}/^{240}\text{Pu}, \times 10^{-3}$	“Age”, years
Pu 1	0.11 ± 0.01	3.9 ± 0.2	0.35 ± 0.05	3.4 ± 0.5
Pu 2	0.38 ± 0.03	13.4 ± 1.3	1.60 ± 0.31	15.3 ± 2.4
Pu 3	0.25 ± 0.03	8.8 ± 1.3	1.21 ± 0.20	11.4 ± 1.6

Two values of the plutonium “age”, calculated on the basis of two different isotopic ratios for each of the three microparticles, are the same within the range of errors. Assumptions for the equal coefficients of ionization for uranium and for plutonium are not obvious. Corrections for the ionization differences can be made relative to the results of ICP-MS measurements. Coefficients of ionization for uranium and for plutonium are the same and close to 100% for this method. Measuring a ratio $^{236}\text{U}/^{240}\text{Pu}$ without preliminary chemical separation is also carried out as part of this research work. Remnants of three microparticles, which remained after SIMS analysis, were used for ICP-MS preparations. Measurement results are presented in Table 3.

TABLE 3. AGE OF PLUTONIUM IN MICROPARTICLES, ESTIMATED BY USING ICP-MS MEASUREMENTS

Particle ID	$^{236}\text{U}/^{240}\text{Pu}, \times 10^{-3}$	“Age”, years
Pu 1	0.44 ± 0.06	4.2 ± 0.6
Pu 2	1.75 ± 0.14	16.6 ± 1.3
Pu 3	1.33 ± 0.15	12.5 ± 1.4

Comparison of the “ages” of plutonium, estimated by the use of SIMS and ICP-MS analysis results demonstrates systematic underestimation of values calculated on the basis of SIMS measurements under the assumption of equal coefficients of the ionization for uranium and for the ionization of

plutonium. A more precise analysis is the subject of additional work, but it is clear that age of materials can be determined using the results of analysis of microparticles found on the fibers.

The possibility and results of the measurements of trace element concentrations (no more than 1 mg per 1 g of uranium) in individual microparticles by using ICP-MS depends on several parameters: i) the size of the microparticle, ii) the concentrations and ionization coefficients of the measured elements as well as iii) the abundance and content of the measured elements. Therefore model estimations are carried out in this research work to estimate the minimal detectable concentrations of different chemical elements in uranium microparticles using inductively coupled plasma mass spectrometry. The detection limits have been calculated for 64 chemical elements during the analysis of spherical uranium oxide microparticles with sizes: 10 μm , 20 μm , 50 μm and 100 μm .

Analysis of calculated data allows for the conclusion that any of the 64 considered chemical elements can be determined at the trace level in the UO_2 particle with equivalent diameter of 100 μm . Only 6 elements: calcium, iron, manganese, rubidium, selenium and zinc, cannot be determined in the particle with the equivalent diameter of 50 μm . Nineteen more elements cannot be determined in a particle with the equivalent diameter of 20 μm . Fifteen trace elements: aluminum, boron, germanium, hafnium, molybdenum, niobium, lead, platinum, rhenium, antimony, tin, tantalum, thorium, titanium and thallium can be determined in a particle with an equivalent diameter of 10 μm .

3. CONCLUSIONS

Techniques for the detection, localization on fabric, preliminary characterization and removal of alpha-emitting microparticles from fabric for further analyses are developed and experimentally verified. Sizes of detectable microparticles depend on the radioactivity of alpha-emitting isotopes within the microparticle. The typical minimal size of a plutonium microparticle is 0.1 μm and the minimal size of a uranium microparticle is about 1 μm .

Preliminary characterization allows for the determination of uranium and/or plutonium in microparticles and an estimate of their amount with an error of no more than 20%.

The effectiveness of isotopic analysis of plutonium in microparticles by secondary ion mass spectrometry is confirmed. The relative error of measurement of plutonium isotopes content is about 0.1% for a content of about 1 picogram and is about 0.5% for the content of about 10 femtogram.

The relative error of plutonium dating in microparticles with an equivalent diameter of approximately 3 μm using a secondary ion mass spectrometer is about 10% for an age of about 20 years. Additional information about the ratio of ionization coefficients is necessary for numeric age estimations.

The minimal detectable concentrations by ICP MS instrument ELEMENT 2 of different chemical elements in uranium microparticles are estimated. These minimal concentrations are different for different elements and depend also on the size of the microparticle and on the list of determined elements.

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DEVELOPMENT OF A GAMMA-SPECTROMETRIC PROCEDURE FOR THE IDENTIFICATION OF URANIUM AND PLUTONIUM IN THE PRESENCE OF GAMMA-EMITTING RADIONUCLIDE MARKERS INDICATIVE OF SPENT NUCLEAR FUEL (SNF) OUT OF REGULATORY CONTROL

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1. INTRODUCTION

The data presented below represents a brief description of the work conducted to date. It is expected to create an independent approach for the use of non-destructive analytical methods applied to spent nuclear fuel. The presence of γ -markers should theoretically indicate that the studied sample contains nuclear material and fission products. For example, a peak of ^{241}Am γ -radiation can be regarded as indirect evidence of plutonium presence in a sample, because the radioactive decay of ^{241}Pu ($t_{1/2} = 14.4$ years) results in the appearance of americium nuclei. The presence of plutonium in the sample, in turn, may indicate that the sample contains irradiated uranium.

Prior to exposure in a reactor, nuclear fuel can be characterized by γ ray and neutron measurements. However, after long exposure of fuel under a neutron flux in the reactor the presence of uranium and plutonium is significantly masked by radiation from fission products and transuranic elements. For example, γ -radiation of plutonium can be observed only as a broadening of uranium isotopes lines. The proposed non-destructive method is based on the finding of indirect evidence of the presence of uranium and plutonium in the samples by γ rays of radioactive fission products.

The following radionuclides are identified here as γ -emitting radionuclide markers (not short-lived): ^{137}Cs , ^{134}Cs , ^{106}Ru , ^{144}Ce , ^{125}Sb , ^{154}Eu and ^{155}Eu . The ratio of these radionuclides' activities limits the number of nuclear devices where the samples could potentially have been irradiated.

All proposed radionuclides are products of nuclear materials fission by neutrons in the reactor core. Therefore, their presence or absence in studied materials, and, if available, their combinations and ratios of activities in γ -spectra can be helpful to draw conclusions about the origin and history of the sample.

The most interesting results for identification of material affected by a neutron flux in the reactor can be obtained from the study of spent nuclear fuel (SNF). Therefore, our attention is focused primarily on the investigation of γ -spectra obtained from different archival samples obtained from SNF. All archival SNF samples already contain known quantities of the uranium-plutonium fuel. This work further allows confirmation of metrological capabilities of the analytical method in addition to the opportunity to obtain information on the correlation between SNF radionuclide composition with the type of nuclear reactor and the associated burn-up of the fuel.

Studies on SNF nuclide composition by destructive methods have been carried out in VG Khlopin Radium Institute for almost fifty years [1-6]. The data obtained were used to develop non-destructive methods for measuring burn-up as well as experimental verification of computer programs written for SNF nuclide composition calculations.

2. WORK CONDUCTED

2.1 INSTRUMENTAL

The gamma spectrum, which includes characteristic spectral lines of nuclides and is typical for irradiated nuclear material, does not always display the sufficient accuracy because of insufficient energy resolution and/or low intensity. Therefore measurements were made with the help of two different devices:

The first measurement employed a digital γ ray spectrometer DSPEC jr. 2.0TM with ORTEC high purity Germanium (HPG) planar photon detector system. This detector is designed to register γ rays with energies of 3 - 300 keV. It has a complete absorption in the energy range of 5 - 120 keV. The obtained spectra were saved and interpreted by MAESTRO[®]-32 software and "by hand".

The second measurement was made using a digital γ ray spectrometer with ORTEC high purity Germanium (HPG) coaxial detector system. This detector is designed to register γ rays with energies over 100 keV with efficiency up to 20%. The obtained spectra were saved and interpreted by EcoGamma[®] software.

2.2 KEY RESULTS

Experimental data obtained from reference samples of regenerated uranium and two SNF samples from two nuclear power plants in Russia are presented below. The history of these samples, their isotopic composition at the time of reactor shutdown (i.e., the end of neutron irradiation) and the data on the calculated and experimentally determined fuel burn-up are summarized below:

2.2.1 Reference Samples

2.2.1.1 Regenerated uranium dioxide from SNF

Regenerated uranium dioxide (0.56 g) after SNF reprocessing. Table 1 compiles the isotopic content (mass %).

TABLE 1. SPECIFIC CONTENT OF URANIUM ISOTOPES

Isotope	Atomic content, %	Mass content, %
²³² U	$(9.40 \pm 1.45) \cdot 10^{-8}$	$(9.16 \pm 1,42) \cdot 10^{-8}$
²³⁴ U	0.011164 ± 0.000048	0.010978 ± 0.000468
²³⁵ U	0.952248 ± 0.009595	0.94035 ± 0.00948
²³⁶ U	0.192562 ± 0.002177	0.190966 ± 0.002159
²³⁸ U	98.8440 ± 0.0098	98.8577 ± 0.0098

Using SNF characteristics, the amount of SNF burn-up degree (Table 2) can be calculated based on chemical and physical analysis using three methods:

- (1) measuring the reduction of the total number of heavy elements atoms in the fuel as a result of irradiation;
- (2) measuring ratios of chosen heavy isotopes before and after fuel irradiation by calculated equations, including appropriate nuclear constants; and,
- (3) measuring the ratio of the number of atoms or chosen isotope groups (fission products) and their yields in the fission of heavy isotopes.

2.2.1.2 Kalinin WER-1000 SNF samples [7]

A fragment of fuel element № 19 from the fuel assembly № SV0013.

Initial enrichment in the fuel assembly – 3.9%.

Upload – 20.08.1998.

Shutdown – 13.06.2004.

Storage before γ -spectrometric measurements – 12 years.

Calculated fuel burn-up degree (the NPP certificate characteristics) – $51.86 \text{ GW}\cdot\text{day}\cdot(\text{t U})^{-1}$.

TABLE 2. SPECIFIC CONTENT OF U AND PU ISOTOPES IN THE SNF SAMPLE ON THE DATE OF REACTOR SHUTDOWN (13.06.2004)

Isotope	Content, kg·(t U) ⁻¹
²³⁸ U	990.67 ± 0.04
²³⁶ U	6.27 ± 0.03
²³⁵ U	2.904 ± 0.017
²³⁴ U	0.158 ± 0.016
<hr/>	
²³⁸ Pu	0.68 ± 0.03
²³⁹ Pu	6.18 ± 0.07
²⁴⁰ Pu	3.77 ± 0.05
²⁴¹ Pu	2.08 ± 0.05
²⁴² Pu	1.84 ± 0.04

The fuel burn-up degree was determined experimentally by various methods (Table 3), where

W_{MTA} refers to the method of heavy atoms,

W_{137} – measurements of ¹³⁷Cs specific content in the sample,

W_{148} – measurements of ¹⁴⁸Nd specific content in the sample;

$W_{5/8}$ – calculations of the ratio of ²³⁵U/²³⁸U relative masses;

$W_{4/7}$ – calculations of the ratio of ¹³⁴Cs/¹³⁷Cs relative activities

W_C – the average value of the fuel burn-up degree.

It is clear that values of the fuel burn up degree, obtained by four methods (W_{MTA} , W_{137} , $W_{5/8}$ and W_{148}) agree with each other within the limits of measurement error.

TABLE 3. VALUES OF THE FUEL BURN UP DEGREE OBTAINED BY DIFFERENT METHODS

W_{MTA}	W_{137}	W_{148}	$W_{5/8}$	$W_{4/7}$	W_C
69.0 ± 1.9	67.5 ± 2.4	66.5 ± 2.2	67.7 ± 1.8	55 ± 3	67.7 ± 1.9

Differences between the amount of the fuel burn-up degree, obtained by different methods, may be explained by gas permeability of the fuel element, from which the fuel sample was obtained (part of the ¹³⁷Cs has a noble gas parent - ¹³⁷Xe). Taking into account different mechanisms of ¹³⁴Cs and ¹³⁷Cs accumulation by actinide fission, it is obvious that ¹³⁴Cs accumulates in smaller quantities than in the hermetic fuel rod. At the same time, there is practically no influence of gas permeability on the accumulation of ¹³⁷Cs. Thus, the ¹³⁴Cs/¹³⁷Cs activity ratio in the failed fuel element fragment should be lower than in the hermetic fuel rod at the same fuel burn-up degree.

2.2.1.3 A fragment of fuel element № 297 from the fuel assembly № ED0454.

The NPP certificate characteristics:

306 fuel elements with initial enrichment 4.4%.

6 fuel elements with initial enrichment 3.6% + 5% Cd₂O₃.

Upload – 04.08.2003.

Shutdown – 25.08.2007.

Storage before preliminary destructive tests – 2.809 years.

Storage before γ -spectrometric measurements – 9 years.

Calculated fuel burn-up degree – 49.1 GW·day·(t U)⁻¹.

TABLE 4. SPECIFIC CONTENT OF U AND PU ISOTOPES IN THE SNF SAMPLE ON THE DATE OF REACTOR SHUTDOWN (25.08.2007)

Isotope	Content, kg·(t U) ⁻¹
²³⁸ U	990.898 ± 0.089
²³⁶ U	6.346 ± 0.061
²³⁵ U	2.625 ± 0.057
²³⁴ U	0.131 ± 0.032
<hr/>	
²³⁸ Pu	0.741 ± 0.026
²³⁹ Pu	6.076 ± 0.034
²⁴⁰ Pu	3.825 ± 0.031
²⁴¹ Pu	1.835 ± 0.023
²⁴² Pu	1.894 ± 0.024

The fuel burn-up degree was determined experimentally by various methods (Table 5). This table shows, that values of fuel burning-up degree for three methods (W_{137} , W_{148} , W_{146}) are consistent with each other within the measurement error, which is 3.0, 2.8 and 2.7% for these methods, respectively.

Significant differences in the values of the fuel burn-up degree may be associated with the fact that the real value of the initial fuel enrichment does not match passport characteristics, provided by the NPP. It should be mentioned that the most reliable results of the fuel burn-up degree can be obtained by measuring the specific content of neodymium isotopes because the content of fuel fission products depends on the fuel burn-up degree, but does not depend on the history of irradiation, or on the initial uranium enrichment. The results of experiments are: 63.4 ± 1.8 GW·day·(t U)⁻¹ (according to the specific content of ¹⁴⁷Nd) and 61.9 ± 1.7 GW·day·(t U)⁻¹ (according to the sum content of ¹⁴⁵Nd and ¹⁴⁶Nd).

TABLE 5. VALUES OF THE FUEL BURN UP DEGREE OBTAINED BY DIFFERENT METHODS. W_{146} IS CALCULATED FOR THE SUM OF ¹⁴⁵ND AND ¹⁴⁶ND SPECIFIC CONTENT IN THE SAMPLE.

W_{MTA}	W_{137}	W_{148}	W_{146}	$W_{4/7}$	W_C
72.1±7.0	63.4±1.9	63.4±1.8	61.9±1.7	16.9±0.7	62.8±1.8

Sample gamma-spectra of the regenerated uranium dioxide from SNF (Figs 1, 2) and fragments (Fig 3) of the fuel element from VVER1000 fuel assembly (2 spectra) are presented below.

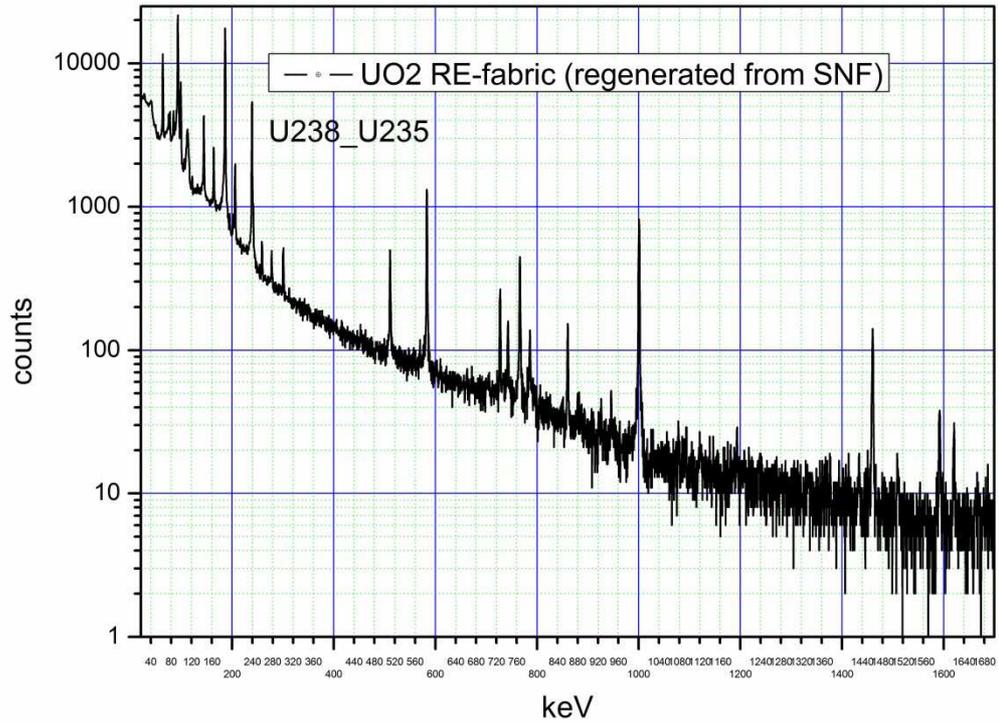


FIG 1. Complete spectrum of the regenerated uranium dioxide from SNF.

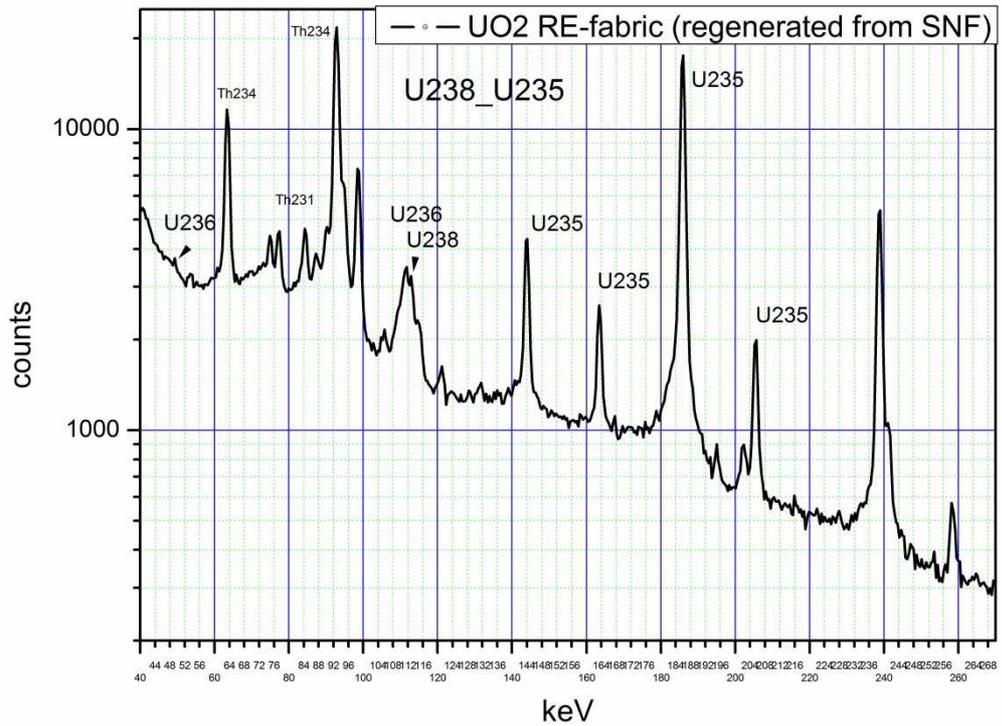


FIG 2. Nuclear analysis of the regenerated uranium spectrum. Low energy part of gamma spectrum.

In the regenerated uranium spectrum (Fig. 2) the ^{235}U lines are definitely presented and traces of lines of ^{236}U and ^{238}U , daughters of ^{238}U – ^{234}Th , $^{234\text{m}}\text{Pa}$ and ^{236}U daughters – ^{212}Pb , ^{212}Bi , ^{208}Tl can also be found.

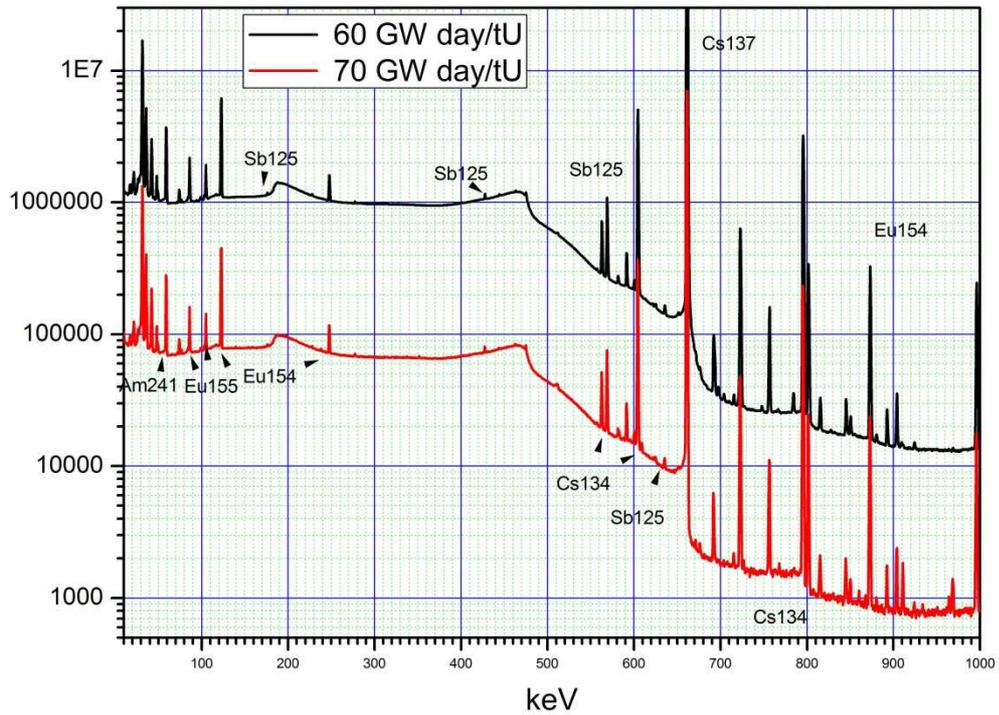


FIG 3. Sample spectra of the fragments of the VVER1000 SNF.

SNF spectra (Fig. 3) show lines of the ^{241}Am , fission products – ^{155}Eu , ^{154}Eu , ^{125}Sb , ^{134}Cs , ^{137}Cs , and traces of lines of ^{231}Th and ^{237}Np . Lines of ^{40}K , ^{60}Co correspond to background.

3. CONCLUSIONS

Preliminary studies of the spectra, obtained by gamma spectrometry using planar and coaxial detectors demonstrate the possibility of the determination of the presence or absence of U and/or Pu in irradiated samples with a known nuclide composition.

Experimental data, presented in this short report, along with other available information obtained by destructive analytical methods as well as from the expected results of spectrometry will form the basis for the development of methodology for the rapid analysis of irradiated materials relative to nuclear materials from which they originated.

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DEVELOPMENT OF THE TRACE ELEMENT TECHNIQUE FOR THE MEASUREMENT OF THE CHARACTERISTIC IMPURITIES OF U_3O_8 FOR IDENTIFICATION PURPOSES IN THE ILLICIT TRAFFICKING OF NUCLEAR MATERIALS

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1. INTRODUCTION

This summary report was edited by the IAEA and is an extract of a full report submitted by the chief scientific investigators [1]. The aim of this research is to develop a specific trace analysis technique for identification of uranium ore concentrate samples seized from illicit trafficking. Ore concentrates chemically are uranyl uranate (U_3O_8) with a larger or smaller content of various impurities. Samples of ore concentrates do not constitute a serious danger in the context of radiologic terrorism due to their lower relative radioactivity. At the same time, these kinds of nuclear materials constitute a threat in terms of nuclear non-proliferation because nuclear material control and accounting for these materials are incomplete. Finished products of ore processing enterprises (uranium concentrates) are accountable for material accountancy purposes, but not semi-finished products situated at ore fields and such enterprises. Trace analysis is a common way to identify ore concentrate samples seized from illicit trafficking [2]. Laboratories involved in trace analysis of uranium ore concentrates usually use some variations of ASTM C 1287-03 technique [3,4]. However this technique was not originally designed for the purposes of identification of uranium ore concentrates and there is no indication that it is the best solution.

The main problem in uranium trace analysis by mass spectrometry is a strong matrix effect. There are several alternative solutions to compensate for this effect during inductively coupled plasma mass spectrometry (ICP-MS) measurement: an internal standard method, an external standard method, a great (i.e. 'infinite') dilution method, and a chromatography method. The ASTM C 1287-03 technique utilises a combination of external and internal standard methods to overcome this suppression effect. In addition to the ASTM C 1287-03 technique, there is an ASTM C 1647-06 technique which describes the preparation of nuclear material samples for trace analysis by a chromatography method [5]. This technique is not widely used, but still there are some published references on its usage [6, 7]. However, its utility in the identification of uranium material is not yet evaluated.

In the course of studying seized nuclear materials, it is impossible for a researcher to specify the true origin of a sample under investigation until the completion of the examination. Origins of U_3O_8 may vary to include: ore, ore concentrate, a semi-finished product of uranium processing or a nuclear-grade product. Depending on its origin, U_3O_8 will contain different impurities and concentrations. Therefore, it is advantageous to develop a common analytical technique for U_3O_8 trace analysis applicable to uranium materials of any possible origin. In order to develop this procedure, it is necessary to first list possible impurities of U_3O_8 of different origin. In this IAEA Research Contract, a list of characteristic impurities in uranium materials has been compiled by means of a review of literary data. Four ICP-MS methods of uranium materials trace analysis have been tested in order to determine their features and to develop a best practice for U_3O_8 trace analysis and origin identification.

2. WORK CONDUCTED

2.1 EXPERIMENTAL

This work was carried out by means of an inductively coupled plasma quadrupole mass-spectrometer. The mass-spectrometer is equipped with a collisional cell that can operate in kinetic energy discrimination mode (KED mode). All tests were carried out at standard resolution 0.75 a.m.u. in KED mode to minimize polyatomic interference. Helium gas was used to feed the collisional cell (99.9999% grade), the ion source was fed with argon (99.998% grade). The mass-spectrometer was equipped with ion source nickel cones, a nebulizer chamber thermostat and a kit of hydrofluoric acid resistant components: sapphire injector, concentric nebulizer and cyclone spray chamber made of PFA-plastic material.

The following chemicals were used for preparation of sample and calibration solutions: deionized water, suprapure nitric acid, suprapure hydrochloric acid and double-distilled hydrofluoric acid (subboiling distillation in a teflon still). Calibrating solutions necessary to determine the sensitivity of the device were made of high-purity standards 48-element standard solution ICP-MS-68A-A and 13-element standard solution ICP-MS-68A-B. Single-element stock solutions of Sc, Rh and Re were used for internal standard preparations. To ensure solution stability of some elements a small amount of hydrofluoric acid was added to digestion, calibration and other solutions. All experiments were conducted in duplicate: Si, Ti, Mo, Sn, W and similar elements were analyzed with addition of HF while other elements were analyzed with HF-free solutions.

To control validity of the results, a set of U_3O_8 standard reference materials GSO 7678-99 "SOU FD" were used. It consists of 6 units and each of them is certified with regard to 23 impurities: Al, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Si, Sn, Ti, V, W and Zn. The 6 units of this set are characterized with the same list of impurities but different concentration values of each. GSO 7678-99 "SOU FD" standard reference materials were produced at Ural Polytechnic Institute (Russia) in 1999 for U_3O_8 trace analysis quality check and awarded with the category "The standard reference material of the State" which is the highest category, according to national laws. SRM digestion procedure was carried out at 200°C for 2 hours in PTFE autoclaves to ensure a complete dissolution of all impurities to include the resistant annealed oxides of BeO, Al_2O_3 , Cr_2O_3 and SnO_2 . Two different acid mixtures were used for sample digestion: 40% HNO_3 + ~2% HCl and 40% HNO_3 + ~2% HF.

Polyethylene test tubes provided with polypropylene caps were used to prepare and handle solutions. A dismountable chromatography column was produced to perform a uranium chromatography separation. All column components except filters and the test tube for eluate collection were made from PTFE. Upper and lower filters were made from a porous kind of PTFE. The column reservoir was filled with 3 ml of UTEVA resin (100-150 μ m particle size). The digested sample was loaded onto the column in 40% HNO_3 solution (for some elements with addition of small amount of HF). The same solution was used to eluate impurities from the column. At the end of the separation process, uranium was removed from the column by a water rinse.

2.2 RESULTS AND DISCUSSION

A comprehensive set of reference data from the literature on U_3O_8 composition of different origin was collected for the present work. This data comprises trace element composition of Olympic Dam, Ranger, Beverley, Mary Kathleen, Elliot Lake, Bancroft, Rossing and Rajska uranium ore concentrates, incorporating typical elemental co-products of "unconformity", sandstone, breccia, conglomerate, vein, intrusive, metasomatic and volcanic uranium ores as well as typical impurities in several types of nuclear grade uranium products in addition to some other sources. Even a brief analysis of this data has shown that practically all elements should be regarded as characteristic during the identification of samples of unknown origin. Practically any element may serve as a unique identifier for U_3O_8 coming from a specific source. For example, it was discovered that uranium ore concentrates of Elliot Lake deposit group contain indium and ores of Witwatersrand deposit group contain platinumoids.

A column calibration was performed in advance of the chromatographic separation of uranium and impurities. Two mixtures of uranium and multi-element standard solutions (ICP-MS-68A-A and ICP-MS-68A-B) were used as samples for column calibrations. After the sample loading, 7 eluate fractions were collected (2 ml each) and the element distribution in each eluate fractions was studied (see Table 1). The majority of the non-actinide elements has no affinity to UTEVA resin and can be collected in the first three free column volumes of eluate. However, it appears that thallium and scandium still have significant affinity to the resin and these elements are present in the first six free column volumes of eluate. Also the great affinity of thorium to the UTEVA resin was demonstrated since it is an actinide [8]. Although the literature [7] declares the possibility of thorium desorption from UTEVA resin alongside of other impurities, the present results do not provide confirmation. Also the gradual washout of phosphorus from UTEVA resin was observed [6]. For this reason, UTEVA cannot be used for sample preparation for measurements of phosphorous concentration.

TABLE 1. ELEMENT DISTRIBUTION BY ELUATE FRACTIONS DURING CHROMATOGRAPHIC SEPARATION OF URANIUM AND IMPURITIES USING UTEVA RESIN FILLED COLUMN

Element or group of elements	Element distribution by eluate fractions, %							Elements in group
	№1	№2	№3	№4	№5	№6	№7	
General	15	60	20	5	0	0	0	Li, Be, B, Na, Mg, Al, Si, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, In, Cs, Ba, Re, Pb, Bi
Titanium	5	60	30	5	0	0	0	Ti, Ge, Zr, Nb, Mo, Ag, Sn, Sb, Te, Hf, W
Lanthanum	14	62	20	4	0	0	0	La
Europium	9	64	21	6	1	0	0	Eu
Lutetium	0	37	39	17	5	1	0	Lu
Yttrium	3	60	26	10	1	0	0	Y
Scandium	0	8	35	28	16	10	4	Sc
Tantalum	1	49	43	7	1	0	0	Ta
Thallium	0	1	3	53	39	4	1	Tl

Lower boundaries of the concentration measurement ranges have been evaluated for four alternative techniques (internal standard, external standard, great dilution and chromatography preparation) by means of standard reference material analyses (Table 2). For all elements except phosphorus the best results come from the chromatography preparation technique. Uranium matrix effects using the internal standard method resulted in incorrect data for some elements (P, Si, Mn, Mo, Ba, Sn and W). It is difficult to choose a suitable internal standard for every element in such cases. Moreover, seized nuclear material can contain a wide range of various impurities that should be treated as analytes for identification purposes, so the correct choice of internal standard becomes difficult. The external standard method applied to compensate for matrix effects provides adequate measurement accuracy for all impurities, but the available measurement range is not the best. The poorest results come from dilution method because uranium matrix effect remains significant even in 40 ppm uranium solutions and required dilution appears too high for real practice. The main features of the four tested alternative techniques are summarized in Table 3.

TABLE 2. LOWER BOUNDARIES OF THE CONCENTRATION MEASUREMENT RANGES FOR DIFFERENT TECHNIQUES ($\mu\text{g/g}$ or ppm)

Element	Internal standard method	External standard method	Great dilution method	Chromatography method
Li	0.27	0.85	26.5	0.27
Be	2.7	8.5	26.6	2.7
B	8.5	8.5	none	0.9
Mg	3.5	9.2	9.2	3.5
Al	8.7	8.7	84.7	2.9
Si	none	27.6	none	27.6
P	none	8.8	841.1	none
K	27.9	27.9	none	0.52
Ca	3.0	8.7	841.1	3.0
Ti	26.6	26.6	26.6	2.7
V	2.7	8.4	2.7	2.7
Cr	8.6	8.6	2.8	2.8
Mn	none	0.9	2.7	0.30
Fe	9.1	9.1	84.7	9.1
Ni	8.9	8.9	3.1	3.1
Cu	2.8	2.8	2.8	0.36
Zn	26.7	8.5	83.9	2.7
Mo	none	8.5	2.7	2.7
Cd	2.7	0.27	2.7	0.1
Sn	none	26.6	83.9	2.7
Ba	none	2.7	8.5	0.3
W	none	8.5	26.7	2.7
Pb	2.7	8.5	2.7	2.7

TABLE 3. MAIN FEATURES OF DIFFERENT TRACE ANALYSIS TECHNIQUES

Method	Measurable elements	Total dilution factor	Relative labor expenditure	Possibility to analyze ^{233}U and ^{236}U based samples
Internal standard	Some elements	850 – this work	average	No
External standard	Any metals and some non-metals (B, Si, P, Ge, As, Se and Te)	850 – this work 425 – [3] 8500 – [2]	average	No
Great dilution	Some elements	42500 – this work	low	Yes
Chromatography	Any metals, except Th, and some non-metals (B, Si, Ge, As, Se and Te)	425 – this work 240 – [5]	high	Yes

3. CONCLUSIONS

All elements traditionally used as internal standards in ICP-MS techniques can be among U_3O_8 impurities depending on the material origin: Be, Sc, Ga, Ge, Y, Rh, In, Cs, Pr, Tb, Ho, Re, Bi, and Th. Therefore, the internal standard method should not be used for the analysis of unknown samples for their identification even as an auxiliary method. Consequently, the ASTM C 1287-03 technique widely used for this purpose can introduce incorrect measurement results since it utilizes Sc and Rh as internal standards [3].

The matrix-match external standard method makes it possible to eliminate matrix effect successively when applied to uranyl uranate samples analysis. This method is equally efficient when applied to various elements. The drawback with this technique is the need to prepare highly-pure uranyl uranate for calibrating solutions. Purification of this substance imposes some restrictions on the range of measurement due to the resulting trace element concentration.

Sample dilution is an unpromising method of eliminating uranium matrix effects. This technique requires dilution of the digested sample additionally by a factor of 200 (minimum) to reduce matrix effect to negligible values. The uranium concentration of the solution must be reduced from 0.9% to <40 ppm (preferably to <10 ppm) to eliminate uranium matrix effects. In this case, 200-fold or 1000-fold dilution results in a similar compromise of the detection limits. The necessity to overcome this drawback is contrary to the efficiency of this method.

The best results in terms of detection limits have been obtained from the chromatography technique of sample preparation for analysis. This method is an improvement by 3 to 50 times relative to the best results gained with the other examined techniques. Chromatography separation allows extraction of at least 56 impurities from the sample with residual uranium content below 0.5 ppm. This uranium concentration produces no essential impact on signal intensities of other elements, so there is no need to add uranium matrix to calibration solutions.

However, measurement of phosphorus concentration is impossible when samples are prepared with the UTEVA resin chromatography method. Phosphorus is gradually washed out from the composition of the resin. Also three elements (Sc, Tl, and Th) can be gradually extracted by repeated washings for analysis from the U_3O_8 by the chromatography method, but this increases required analysis time, the total dilution factor and detection limits.

The best practice for measurement of a wide range of trace elements in U_3O_8 samples of unknown origin is utilization of the chromatography separation procedure of uranium and impurities. This conclusion has been experimentally confirmed in the present work for 22 elements through analysis of six standard reference materials from the GSO 7678-99 set. For some elements (P, Sc, Tl, and Th), it is advisable to perform a separate measurement using the external standard method.

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CONCLUSIONS OF THE COORDINATED RESEARCH PROJECT

Thirteen reports are included in the present research report in the context of the Coordinated Research Project (CRP) J02003 “Identification of High Confidence Nuclear Forensics Signatures for the Development of National Nuclear Forensics Libraries” to include parallel nuclear forensics research undertaken by Russian investigators.

The experts recognized the importance of nuclear forensics to a State’s capacity to prevent and respond as part of a State’s nuclear security infrastructure to incidents of nuclear and other radioactive material out of regulatory control. Nuclear security relies upon science throughout this infrastructure; because of the requirement for consistency with national legislation and international legal instruments, results must be defensible in a court of law or recognized internationally. Nuclear forensics has the additional requirement that the analysis of exhibits or evidence contaminated with nuclear or other radioactive material may be used as part of criminal proceedings concerning unauthorized acts involving such materials. In this regard, nuclear forensics utilizes specialized techniques and complements traditional forensics, and is most likely to be applied in support of and in coordination with law enforcement.

Because more States have developed nuclear forensics capabilities to prevent and respond to a nuclear security event and to address a range of nuclear security threats, the need for validated methodologies and high confidence analysis grows in importance. Coordinated research affords a mechanism for innovation to address new requirements for nuclear forensics to identify the origin of nuclear and radioactive material from all stages of the nuclear fuel cycle as well as to ensure the highest confidence in the findings from an examination.

The coordinated research results build upon existing and established capabilities, techniques and knowledge. Insight into material histories is enabled by the use of existing indigenous capabilities together with subject matter expertise oriented to measuring characteristics in a range of samples derived from the nuclear fuel cycle. Subject matter expertise may exist in government, industry, universities and research organizations. The participants further noted that novel techniques, instrumentation and methods may greatly enhance future nuclear forensic analytical capabilities.

A nuclear forensic signature is a characteristic, or set of characteristics, that can be used to determine the origin or provenance of an unknown nuclear or other radioactive material. Application of nuclear forensic signatures can be used to provide information to help answer the following questions that may be posed during the investigation of a nuclear security event:

- What is the material?
- How was the material produced?
- What was the date of production?
- What is/was the intended use of the material?
- Where was it produced?
- Was a law broken?
- Where was the material lost from regulatory control?
- Is there more material remaining out of regulatory control?

Participants presented findings on the development of new analytical techniques, validation of new applications of existing techniques, the enhancement of existing approaches for the purpose of identifying signatures and the application of existing techniques to materials of local relevance. It was

noted by all researchers that multiple signatures are necessary for building confidence in conclusions made by the nuclear forensic laboratory.

It was acknowledged that research and development is necessary to strengthen the basis of nuclear forensic signatures, to provide validated signatures for materials representing all stages of the nuclear fuel cycle as well as medical radioisotopes and radioactive sources. Different signatures, determined individually but interpreted collectively, may be required to identify from which stage of the fuel cycle the material originated as well as the production history and use of radioactive materials. For this reason, determination of high confidence nuclear forensic signatures supports the identification of nuclear and radioactive materials for which a State is responsible and enables the potential development of a national nuclear forensics library.

As noted in the introduction to this report, the researchers identified four common technical themes from the conduct of the research programme. The ability to link nuclear forensic signatures to specific stages of the nuclear fuel cycle requires i) access to relevant sample materials, ii) the identification of priority signatures, iii) high confidence measurements or predictions, and iv) the ability to perform intercomparisons between data collected on the material of interest and a knowledge base of known material. It was further noted that variations in the materials, signatures, measurements and intercomparisons affect the ability to make unambiguous associations between the signatures and the individual processes within the nuclear fuel cycle.

1. ACCESS TO RELEVANT SAMPLE MATERIALS

Projects undertaken by the participants reflect that the nuclear and other radioactive materials most relevant in a local context are governed by material availability, as well as accessible resources (e.g. analytical and laboratory equipment and subject matter expertise). It was noted that, in particular, studies of uranium ores and ore concentrates, representing the front end of the nuclear fuel cycle, are advantageous since these matrices offer an abundance of isotopic, elemental and physical signatures, are not highly radioactive and pose lesser concerns from a nuclear security perspective. Consideration was given to how elements varied through processing of uranium materials and how the elemental signatures persisted (or not) within this stage of the fuel cycle. With some exceptions (e.g. rare earth elements) it is unlikely that individual signatures persist beyond these initial stages.

Viable elemental and isotopic signatures occur in irradiated fuel. This CRP includes work to build upon earlier findings in the published literature on this material type. Studies are continuing to further understand evolution of various isotopes. Consideration of spent fuel signatures should, where possible, include information on starting fresh fuel composition, reactor type, burn-up and related variables. There were commonalities in two CRP projects where computed compositions were compared and evaluated against experimentally measured values. Optimization of isotopic correlations and their applicability to spent nuclear fuels over a wide range of reactor burn-up values requires further verification.

Nuclear forensic signatures in radioactive sources were further studied. Participants emphasized that forensic methods might assist in the identification of radioactive sources found outside of regulatory control. Distinguishing information may include serial numbers, radioactivity, construction design or signatures determined through different analytical methods. Additional information may be obtained from gamma spectrometry of the activated impurities within the source material.

2. THE IDENTIFICATION OF PRIORITY NUCLEAR FORENSIC SIGNATURES

The goal of the coordinated research was to identify material characteristics, or signatures, that may determine the origin and history of nuclear and other radioactive materials following a nuclear forensics examination. These signatures were obtained from the nuclear forensic analysis of samples taken from uranium ores, uranium ore concentrates, intermediate conversion products and effluents, nuclear fuel pellets, reprocessed and spent nuclear fuel, as well as sealed radioactive sources. Beside laboratory methods, predicative models using data from spent nuclear fuels were used to estimate their provenance (e.g. reactor type, nuclear fuel enrichment and irradiation history). The research results yielded promising outcomes to include:

- For uranium ores, the pattern of rare earth elements (i.e., Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) ratioed to chondrite values are useful to differentiate sources of the ores.
- For uranium ore concentrates, rare earth elements can also be very helpful in identification.
- Furthermore, analysis of uranium ore concentrates by thermogravimetric analysis (heating through 50 - 1000°C) provide unique results for different mine samples.
- Radiochronometry can help to identify uranium nuclear fuels and mixed oxide fuels.
- The fission product inventory can be indicative of the origin of the spent nuclear fuels and provide information of the irradiation history including reactor type and burn-up.
- Trace element signatures may be unique in different sealed radioactive sources; further research on these signatures is warranted.
- Measured and modeled isotope ratios of uranium and plutonium in spent nuclear fuels can be used to discriminate the origin and burn-up history of these materials.

3. HIGH CONFIDENCE NUCLEAR FORENSIC MEASUREMENTS AND PREDICTIONS

Instrumentation and analytical capabilities existing within the State should be applied with certainty to a nuclear forensic examination. A range of sample materials may be encountered, ranging from single particles, to milligrams of powders, to grams of uranium and plutonium bulk oxides as well as sealed radioactive sources. Both unirradiated and irradiated materials may be analyzed to include sealed sources. Of importance, reliable analytical results depend upon documented and validated analytical procedures. Certified reference materials are required for method validation. In addition to customary analytical procedures, new methods are able to exploit novel nuclear forensic signatures.

In this regard, some promising results include improvements to reduce interferences associated with the measurements of lanthanides involving chromatographic separations. New isotopic methods utilize $^{34}\text{S}/^{32}\text{S}$ ratios to resolve differences in sulphate added during in-situ leaching of uranium ores to that originally present. Morphological studies of the uranium ore conversion process indicates different particle sizes and shapes for ammonium diuranate, ammonium uranyl carbonate, uranium peroxide, sodium diuranate and uranyl hydroxide. Techniques to include infrared spectroscopy, diffuse reflectance spectroscopy, microRaman spectroscopy as well as thermogravimetric analysis can identify different uranium ore concentrate types. High fidelity modeling of uranium and/or plutonium isotopic ratios can uniquely separate spent fuel sourced from pressure water reactors, boiling water reactors and liquid metal fast breeder reactors using different starting fuel compositions of uranium, uranium-gadolinium fuels and plutonium.

4. THE ABILITY TO PERFORM INTERCOMPARISONS SUPPORTING NUCLEAR FORENSICS INTERPRETATION

The research clearly emphasized the need for knowledge bases to be available to subject matter experts to aid in nuclear forensics interpretations. The more comparative information available in these knowledge bases allows for greater differentiation of sample histories and origins. Understanding of the pedigree of the data that constitutes these databases is also important; often nuclear forensics data was collected at earlier times and for other purposes than exclusively for the purposes of a knowledge base or development of a national nuclear forensics library. The population of data into a knowledge base is an on-going process; comparative tools always need to be maintained and new data added. National nuclear forensics libraries – to include computational structures for retrieval and statistical comparisons - are in place or being developed by States that utilize existing compilations of data maintained by nuclear regulators, producers and operators. The libraries may be useful to help determine the identity of unknown samples encountered as part of a nuclear security investigation. However, the strength of the knowledge bases reflects the quantity and quality of the comparative data contained within. The experience of chief scientific investigators in establishing a national nuclear forensics library is useful to those contemplating developing a knowledge base to facilitate nuclear forensic interpretations.

5. RESEARCH ACHIEVEMENTS

This coordinated research indicates that analytical and computational tools can be used to identify high confidence signatures reflecting the origin and history of nuclear and radioactive materials. Applied to samples of mined and leached uranium ores, uranium ore concentrates, intermediate compounds from uranium conversion, nuclear fuel pellets, irradiated spent and reprocessed nuclear fuels and radioactive sources obtained internationally, this work demonstrates that a nuclear forensics examination can resolve different origins of samples representing the same stage of the nuclear fuel cycle. Single signatures are likely to be insufficient in determining provenance. Multiple signatures build confidence in nuclear forensic findings; if each signature independently provides information to include or exclude a possible origin, taken together, there is a great likelihood of an unequivocal result supporting the investigation. Consequently, consideration should be given to which groups or pairs of signatures are most valuable in combination. The research conducted here provides an abundance of new characteristics that have been successfully applied as part of a nuclear forensics examination.

The need to focus on the science of nuclear forensics and nuclear forensic signatures is driven by innovation required to exploit nuclear forensic exhibits and evidence and provide certainty on the origin of nuclear and other radioactive materials. As part of the research, subject areas identified for future study may include:

- Methods and techniques for analysis and interpretation for the identification of seized nuclear and other radioactive materials using forensically significant information.
- Traditional forensics analysis (e.g. fingermarks, hairs, fibers, deoxyribonucleic acid (DNA), toolmarks, explosive and gunshot residues, digital evidence, pollens, dust, questioned documents) found associated with materials contaminated by radionuclides.
- Forensic analysis of radioactive sources to include non-destructive and destructive analytical techniques to determine radiogenic and non-radiogenic characteristics, relevant origin and history, age dating, and interpretation of results using comparisons with databases maintained by source regulators and others.

Other topics for research noted by the experts included investigations of microparticles (between 0.1 to 100 microns in size) to identify robust signatures within, as well as studies to investigate the homogeneity and age dating of microparticles (to include those from urban dust). Additionally, a focus on improved methods for nuclear forensic age dating of nuclear and other radioactive materials

(analytical methods, analytical standards) as well as microstructural analysis of nuclear materials (to include studies of uranium ore concentrates and microparticles) were suggested.

Scientific discovery and research is a vital element of a sustainable programme in nuclear forensics, and research promotes the validation of techniques, approaches and signatures for effective use as part of a comprehensive nuclear security infrastructure. As more States both contemplate and develop national nuclear forensics capabilities, the demands on the science supporting nuclear forensics will increase to best address law enforcement and nuclear security requirements as well as the necessary confidence in the findings from an examination.

APPENDIX I

. CONTRACTS AND AGREEMENTS: IAEA COORDINATED RESEARCH PROJECT ON
 “IDENTIFICATION OF HIGH CONFIDENCE NUCLEAR FORENSICS SIGNATURES FOR THE
 DEVELOPMENT OF NATIONAL NUCLEAR FORENSICS LIBRARIES”; (C) = FUNDED
 CONTRACT AND (A) = AGREEMENT

Research Institution	Chief Scientific Investigator	Title
Australian Nuclear Science and Technology Organisation Australia	E. Keegan A. Wotherspoon	Investigation of Various Signatures and their Application to the Provenancing of Materials at the Front End of the Nuclear Fuel Cycle (A)
Instituto de Pesquisas Energéticas e Nucleares Brazil	J. De Souza Sarkis	Investigation of Nuclear Forensics Signatures in Environmental Samples (C)
Canadian Nuclear Laboratories Canada	F. Dimayuga	Nuclear Forensics Signatures of Irradiated CANDU Fuel (A)
European Commission Directorate for Nuclear Safety and Security Joint Research Centre Germany	M. Wallenius	Propagation of Nuclear Forensics Signatures at the Front-End of the Fuel Cycle (A)
Department of Electrical and Computer Engineering Demokritus University of Thrace Greece	G. Nikolaou	Parameterization of Unknown Spent Nuclear Fuel from Nuclear Reactors in View of Identifying its Origin (C)
Centre for Energy Research Hungarian Academy of Sciences Hungary	É. Kovács-Széles	Establishment of a National Library for Nuclear Forensics Purposes in Hungary (C)
Bhabha Atomic Research Centre India	S.K. Aggarwal	Mass Spectrometry, Radiometry and other Analytical Techniques for Nuclear Forensics (A)
National Nuclear Energy Agency- BATAN Indonesia	B. Briyatmoko	Identification of High Confidence Nuclear Forensics Signatures for Mining, Milling and Conversion Processes (C)
Center for Applied Radiation Science and Technology (CARST) North-West University (Mafikeng) South Africa	M. Mathuthu	Application of ICP-MS and Isotopic Techniques in Resolving Nuclear Forensics Signatures in Uranium Mining and Processing (C)
Swedish Defence Research Agency (FOI) Sweden	H. Ramebäck	Measurement of Lanthanides in Uranium Matrices (A)

APPENDIX II

CONTRACTS WITH THE RUSSIAN FEDERATION

Research Institution	Chief Scientific Investigator	Title
Laboratory for Microparticle Analysis	V. Stebelkov	Development of Techniques for Detection and Subsequent Analysis of Alpha-Emitting Microparticles on Fabrics
V.G. Khlopin Radium Institute	V.N. Dushin	Development of a Gamma-Spectrometric Procedure for the Identification of Uranium and Plutonium in the Presence of Gamma-Emitting Radionuclide Markers Indicative of Spent Nuclear Fuel (SNF) out of Regulatory Control
A.A. Bochvar High Technology Research Institute of Inorganic Materials (SC 'VNIINM')	A.Y. Kramchaninov	Development of the Trace Element Technique for the Measurement of the Characteristic Impurities of U_3O_8 for Identification Purposes in the Illicit Trafficking of Nuclear Materials

LIST OF ABBREVIATIONS

ADU	ammonium diuranate
AS	alpha spectrometry
AU	ammonium urinate
AUC	ammonium uranyl carbonate
BNLNFS	Brazilian Network of Laboratories on Nuclear Forensic Science
BWR	boiling water nuclear reactor
CNEN	Comissão Nacional de Energia Nuclear (Brazil)
CRP	Coordinated Research Project
CRM	certified reference material
DA	destructive analysis
DNA	deoxyribonucleic acid
DRS	diffuse reflectance spectroscopy
DU	depleted uranium
EC	European Commission
EDS	energy dispersive X ray spectrometry
EOI	end-of-irradiation
FTIR	Fourier transform infrared spectroscopy
GDMS	glow discharge mass spectrometry
GICNT	Global Initiative to Combat Nuclear Terrorism
HEU	high enriched uranium
HPGe	high-purity germanium
HRGS	high resolution gamma spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
IC	ion chromatography
ILC	identification, localisation and categorization
IR	infrared spectroscopy
ISO/BIPM	International Organization for Standardization/Bureau International des Poids et Mesures
ITDB	IAEA Incident and Trafficking Database
ITWG	Nuclear Forensics International Technical Working Group
JRC	European Commission's Joint Research Centre
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LA-ICP-SFMS	inductively coupled plasma sector field mass spectrometry
LEU	low enriched uranium
LIBS	laser induced breakdown spectrometry
LMFBR	liquid metal fast breeder reactor
LSC	liquid scintillation counting
MBq	megabecquerel
MC-ICP-MS	multi collector inductively coupled plasma mass spectrometry
MGA	Multi-Group Analysis
MLR	multiple linear regression
MOX	mixed oxide
MSP	microspectrophotometry
MTR	Materials Test Reactor
NAA	neutron activation analysis
NCC	neutron coincidence counting
NDA	non-destructive analysis
NFC	nuclear fuel cycle
NIST	National Institute of Standards and Technology

NNFL	national nuclear forensics library
NU	natural uranium
PCA	principal component analysis
PCR	principal component regression
PIE	post irradiation examination
ppm	parts per million
PLSR	partial least squares regression
PWR	pressurized water nuclear reactor
RCM	Research Coordination Meeting
RDD	radiological dispersal device
REE	rare earth element
RSD	relative standard deviation
RSF	relative sensitivity factor
SDU	sodium diuranate
SEM	scanning electron microscopy
SIMS	secondary ion mass spectrometry
SME	subject matter expert
SN-ICP-MS	solution nebulization inductively coupled plasma mass spectrometry
SQL	Structured Query Language
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TIMS	thermal ionization mass spectrometry
U	uranium
UH	uranyl hydroxide
UP	uranium peroxide
UV	ultraviolet
UOC	uranium ore concentrate
WDS	wavelength dispersive X-ray spectrometry
WOBI	WIMS ORIGEN Burn-up Integration
XRD	X-ray diffraction
XRF	X-ray fluorescence

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